

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :

G02B 6/10, C03B 37/022

A1

(11) International Publication Number:

WO 98/26315

(43) International Publication Date:

18 June 1998 (18.06.98)

(21) International Application Number: PCT/US97/22760

(22) International Filing Date: 12 December 1997 (12.12.97)

(30) Priority Data:

60/032,961 13 December 1996 (13.12.96) US
08/956,177 22 October 1997 (22.10.97) US

(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; SP-FR-02-12, Corning, NY 14831 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DAWES, Steven, Bruce [US/US]; 4 East 4th Street, Corning, NY 14830 (US). JOHNSON, Ronald, Edgar [US/US]; P.O. Box 436, Tioga, PA 16946 (US). MASCHMAYER, Richard, Orr [US/US]; 10287 Powderhorn Drive, Corning, NY 14830 (US). SHOUP, Robert, Donald [US/US]; 658 East Lake Road, Hammondsport, NY 14840 (US).

(74) Agents: RUBENSTEIN, Kenneth; Meltzer, Lippe, Goldstein, Wolf & Schlissel, P.C., 190 Willis Avenue, Mineola, NY 11501 (US) et al.

(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

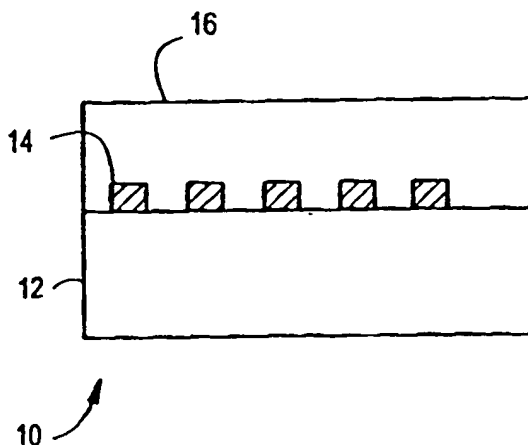
Published

With international search report.

(54) Title: HYBRID ORGANIC-INORGANIC PLANAR OPTICAL WAVEGUIDE DEVICE

(57) Abstract

A planar optical device is formed on a substrate (12) and comprising an array of waveguide cores (14) and a cladding layer (16) formed contiguously with the cores. At least one of the array of waveguide cores (14) and the cladding layer (16) is an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon being directly bonded to substituted or unsubstituted hydrocarbon atoms. In accordance with other embodiments of the invention, a method of forming an array of cores comprises the steps of preparing a core composition precursor material; partially hydrolyzing and polymerizing the material; forming an array of waveguide cores under conditions effective to form an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon being directly bonded to substituted or unsubstituted hydrocarbon atoms.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

HYBRID ORGANIC-INORGANIC PLANAR OPTICAL WAVEGUIDE DEVICE

Related Applications

5 This application claims the benefit of U.S. Patent Application Serial
No. 60/032,961 filed on December 13, 1996 entitled "METHODS AND
COMPOSITIONS FOR CONNECTING OPTICALLY TRANSMISSIVE
MATERIALS" by S. Dawes, which is incorporated by reference, and U.S.
Patent Application Serial No. 08/956,177 filed on October 22, 1997
10 entitled "OPTICALLY TRANSMISSIVE MATERIAL AND BOND" by S.
Dawes and A. Sadd, which is incorporated by reference.

Field of the Invention

15 The present invention relates to a planar optical waveguide device in
which one of the layers is formed according to a hybrid inorganic-organic
material processing method. In particular, one of the layers is an
inorganic-organic hybrid material that comprises an extended matrix
containing silicon and oxygen atoms in which a fraction of the silicon

atoms are directly bonded to substituted or unsubstituted hydrocarbon moieties. The present invention also relates to a method for forming a planar optical waveguide device without the use of a lithographic process. Preferably, the inorganic-organic material comprises a solid material comprised of methyl-siloxane groups, phenyl-siloxane groups, and fluorine which is provided by thermally curing a precursor mixture comprised of polydimethyl-siloxane, methyl trialkoxy silane, phenyl trialkoxy silane, and a structural modifier including a fluorine atom.

Background of the Invention

A typical planar optical waveguide device includes a planar substrate, an array of waveguide cores supported on the planar substrate and a cladding layer. Optical radiation propagates in the cores. The lower index cladding layer confines the radiation to the higher index cores. In some cases, there is a second cladding layer between the cores and the planar substrate.

The planar optical waveguide device is designed to transport optical radiation across a two dimensional planar substrate surface. The device usually performs a passive function on the optical radiation so as to modify the output signal from the input signal in a particular way. Some examples of planar optical waveguide devices are as follows. Optical splitters divide the optical signal power in one waveguide into two or more waveguides. Couplers add the optical signal from two or more waveguides into a smaller number of output waveguides. Spectral filters.

polarizers, and isolators may be incorporated into the waveguide design. WDM (Wavelength Division Multiplexing) structures separate an input optical signal into spectrally discrete output waveguides, usually by employing either phase array designs or gratings. A particular advantage of planar optical waveguide devices is the ability to include multiple functions on one platform. Active functionality can also be included in planar designs, where the input signal is altered by interaction with a second optical or electrical signal. Examples of active functions include switching (with electro-optic, thermo-optic or acousto-optic devices) and amplification.

In general, the key attributes for planar waveguide devices are optical loss, and process capability and cost. Process capability means the ability to write desired pattern of waveguide structures with good resolution and no flaws. Each device has its own specifications, which have to be met in addition to the more generic requirements.

To achieve planar optical waveguides, the current state of the art typically employs the following general process. First, a substrate is provided. The substrate is either silicon or silica, and is provided as a clean flat and smooth surface. In the case of a silicon substrate, a clad coating (a low index silica or silicate) is deposited. Next, a high index core layer (a silicate) is deposited on the substrate, with accurate thickness. The core and clad layer coatings are made from a flame hydrolysis technique, or a CVD technique or a plasma deposition technique. Next, the planar core layer is patterned to form an array of waveguide cores

usually by some variation of a lithography/etch process. Finally, a low index clad layer is deposited to complete the waveguide structure. All of the variations on these process steps share an intrinsic high cost. Deposition times are long and patterning technologies are painstaking. The process is capable of forming high quality structures, with feature resolution of as low as 0.5 microns and low defect counts. In high value added applications such as WDM devices the process has shown some commercial feasibility. In other applications such as couplers however, costs are too high to compete with other technologies.

In view of the foregoing, it is an object of the invention to provide a planar optical waveguide device which overcomes the problems of the prior art. More specifically, it is an object of the invention to provide a planar optical waveguide device that is formed from a low-cost optical material with low absorbance, having a range of indices of refraction and that can be deposited rapidly with a majority of mass loss occurring in the non-solid state. It is also an object of the invention to provide a process for forming a planar waveguide device that obviates the need for lithographic techniques.

Summary of Invention

In accordance with an illustrative embodiment of the invention a planar optical device is formed on a substrate. The device comprises an array of waveguide cores which guide optical radiation. A cladding layer is formed contiguously with the array of waveguide cores to confine the

optical radiation to the array of waveguide cores. At least one of the array of waveguide cores and cladding layer is an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon atoms being directly bonded to substituted or unsubstituted hydrocarbon moieties. This material can be designed with an index of refraction between 1.4 and 1.55 and can be deposited rapidly to thicknesses of up to 40 microns. The material is especially suitable for forming planar waveguide structures because it possesses low optical loss at 1310nm and 1550nm transmission windows. The material is thermally cured from a viscous solvent free state to achieve complete condensation and ultimate elastic properties with minimal mass loss, enabling crack resistance and good shape retention.

In accordance with another embodiment of the invention, a method for forming a planar optical device obviates the need for a lithographic process.

Illustratively, a method for forming an array of cores comprises the steps of:

(1) preparing a waveguide core composition precursor material comprising at least one silane and a source of hydrocarbon moiety, (2) partially hydrolyzing and polymerizing the waveguide core precursor material to form a waveguide core composition, (3) using a mold, forming an array of waveguide cores comprising the waveguide core composition, and (4) completing hydrolysis and polymerization of the waveguide core composition under conditions effective to form an inorganic-organic hybrid

6
material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon atoms being directly bonded to substituted or unsubstituted hydrocarbon moieties. A cladding layer is then deposited over the array of waveguide cores. The use of the mold to pattern the array of waveguide cores obviates the need for a lithographic process. This is a very significant advantage of the invention.

In combination, a complete planar waveguide structure can be made, or if desired, an overclad layer may be provided on a conventionally etched silicate core waveguide array. The primary advantage that can be realized from this invention is cost. The use of the inventive overclad on conventionally patterned glass waveguide arrays can provide advantages. The low process temperature used avoids any deformation of the waveguide cores, whereas high temperature processing can distort the original waveguide shape. The low temperature and low modulus of the inventive overclad also results in low stress fields on the waveguides, so that stress induced polarization effects can be minimized.

Brief Description of the Drawings

Fig. 1 schematically illustrates a planar waveguide device according to the invention.

Fig. 2 schematically illustrates an alternative planar waveguide device according to the invention.

Figs. 3A, 3B, 3C, 3D, 3E, 3F, 3G, 3H, and 3I schematically illustrate preferred methods for patterning an array of waveguide cores according to the invention.

Figs. 4A, 4B, 4C, 4D, and 4E schematically illustrate another preferred method for patterning an array of waveguide cores according to the invention.

Figs. 5, 6, and 7 are near infrared absorbance spectra of the sol-gel hybrid materials.

Detailed Description of the Invention

For purposes of clarity, the detailed description of the invention is divided into the following subsections:

- A. Planar Optical Waveguide Device
- B. Materials Used to Form the Planar Optical Waveguide Device
- C. Specific Example of Materials Used to Form the Planar Optical Waveguide Device
- D. Process for Forming the Planar Optical Waveguide Device
- E. Examples of Planar Optical Waveguide Devices
- F. Spectra of Materials Used to Form Planar Waveguide Devices

A. Planar Optical Waveguide Device

A planar optical waveguide device in accordance with one illustrative embodiment of the invention is shown in cross-section Fig. 1. The device 10 comprises a substrate 12. The substrate 12 may be silicon or silica. A patterned array of waveguide cores 14 is formed on the substrate. Illustratively, the dimension of each waveguide core (height and width) can be as small as 0.5 microns. The waveguide cores 14 can be patterned to form splitters, couplers, filters, WDM devices and devices with other functions as well.

The waveguide cores 14 are covered with a cladding layer 16. In one embodiment of the invention, the array of waveguide cores is a conventionally etched silicate waveguide core array. The cladding layer may be an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms in which a fraction of the silicon atoms are directly bonded to substituted or unsubstituted hydrocarbon moieties.

In an alternative embodiment of the invention, both the array of cores 14 and the cladding layer 16 may be an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms in which a fraction of the silicon atoms are directly bonded to substituted or unsubstituted hydrocarbon moieties. As is explained below, the index of refraction of this material can be designed to provide the high index cores and a low index cladding layer.

In an alternative embodiment of the invention, shown in Fig. 2, a planar optical device 20 comprises a substrate 22, a first cladding layer 24, an array of waveguide cores 26, and a second cladding layer 28. The cladding layers 24, 28 and the array of waveguide cores may all comprise an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms in which a fraction of the silicon atoms are directly bonded to substituted or unsubstituted hydrocarbon moieties, with the index of refraction being chosen for each individual layer.

Preferably, the inorganic-organic material comprises a solid material comprised of methyl-siloxane groups, phenyl-siloxane groups and fluorine which is provided by curing, most preferably by thermally curing, and a precursor material. Preferably, the precursor material comprises a precursor mixture comprised of polydimethyl siloxane, methyl trialkoxy silane, phenyl trialkoxy silane, and a structural modifier with a fluorine atom.

B. Materials Used to Form the Planar Optical Waveguide Device

Practice of the invention further involves preparing a cladding layer and/or a core layer composition precursor material. As is shown in detail below, the precursor material is adjusted depending on whether a core composition or cladding composition precursor material is desired. From the core or cladding composition precursor material, the cladding and core compositions are formed, respectively. These compositions are then used

to form clad layers and arrays of waveguide cores. The precursor material comprises a mixture of hydrolyzable precursors composed essentially of at least one alkoxysilane selected from the group consisting of tetraalkoxysilanes, alkyltrialkoxysilanes and aryltrialkoxysilanes. 5 Optionally, it contains modifiers as noted below.

The mixture may be dissolved in a solvent such as an alcohol and hydrolyzed by addition of acid and water. Alternatively, the precursor mixture may be mixed neat (without solvents) and hydrolyzed by addition of water and optionally acid. The composition is aged while hydrolysis and condensation (polymerization) proceed to form a viscous core cladding 10 composition. This partially hydrolyzed and polymerized material is hereafter termed the core or cladding composition to contrast with the ultimate core or clad wherein hydrolysis and polymerization are essentially complete after curing.

15 It is desirable to drive the hydrolysis and condensation reactions to a sufficient degree so that no precursor is lost during solvent evaporation. Studies have shown that sufficient aging at room temperature for this purpose required on the order of 50 hours. We have found that mild heating of the mixture below 100°C can shorten the time to less than 5 20 hours. In particular, a comparable degree of polymerization (about 80%) was achieved by heating at about 75°C for three hours. Quite surprisingly, gels produced by the accelerated aging process were found less prone to cracking at high heating rates in forming the ultimate clad or core layer.

11
Tetraalkoxysilanes are silicon atoms having four alkoxy groups bound thereto. The four alkoxy groups are usually the same, but this is only for convenience. Alkoxy, as used herein, is meant to include the deprotonated form of any alcohol, including aliphatic alcohols.

5 Alkyltrialkoxysilanes are silicon atoms having three alkoxy groups and one alkyl group bonded thereto. Alkyl is also meant to include arylalkyls. Alkyltrialkoxysilanes suitable for use in the practice of the present invention include, for example, methyltrimethoxysilane ("MTMS") and methyltriethoxysilane ("MTES").

10 Aryltrialkoxysilanes are silicon atoms having three alkoxy groups and one aryl group bonded thereto as used herein, aryl also is meant to include alkylaryl moieties. Aryltrialkoxysilanes suitable for use in the practice of the present invention include, for example, phenyltrimethoxysilane ("PTMS") and phenyltriethoxysilane ("PTES").

15 Preferably, the precursor mixture is comprised of PDMS (polydimethyl siloxane), MTES, and PTES, and preferably further comprises a source of fluorine such as HF and trifluorosilane, and water.

20 The hydrolyzed core or cladding composition can advantageously include other organic components which, on a microscopic level, modify the inorganic network formed by the polymerization of the silane hydrolysis products. The organic component can modify the network with an organo-metallic bond to a silicon atom. Alternatively, the organic component can coexist as an interpenetrating, intermolecular, or

intramolecular network within the inorganic network which does not
attach to a silicon atom.

Suitable organic components which can be incorporated into the
hydrolyzed bonding composition include one or more hydrolysis products
of inert network modifiers, active network modifiers, organic network-
forming modifiers, reactive polymeric modifiers, reactive polymerizable
modifiers, and non-interacting interpenetrating network modifiers.

Inert network modifiers include alkylalkoxysilanes and
arylalkoxysilanes, particularly those having the formula $(R^1)_n(R^2O)_{4-n}Si$,
wherein n is 1, 2 or 3. OR^2 is an alkoxy moiety, such as ethoxy and
methoxy. R^1 can be an alkyl moiety or an aryl moiety, including, for
example, methyl, ethyl and phenyl.

The hydrolyzed core or cladding composition can include from about
0 to about 100 mole%, preferably from about 50 to 100 mole%, more
preferably from about 50 to about 96 mole% of the hydrolysis product of
the inert network modifier, such as the hydrolysis product of
methyltriethoxysilane. Further details with respect to inert network
modifiers can be found in the literature.

Active network modifiers are (substituted alkyl) alkoxysilanes and
(substituted aryl) alkoxysilanes where at least one of the alkyl or aryl
substitutents is a functional group capable of forming complexes with
metal atoms or ions, such as an amino functional group, a mercapto
functional group, or a hydroxy functional group. It is believed that the
functional group promotes surface adhesion of the polymerized core or

cladding composition to inorganic materials. Active network modifiers may also promote adhesion to organic surfaces.

Suitable active network modifiers are those having the formula $(R^3)_n(R^2O)_{4-n}Si$, wherein n is 1, 2 or 3 and wherein OR^2 is an alkoxy moiety. R^3 can be a amine-, carboxy-, mercapto- or hydroxy-substituted alkyl or aryl moiety. The hydrolysis product of the active network modifier is preferably present in an amount from about 1 to about 25 mole%.

As indicated above, the hydrolyzed core or cladding composition can also include one or more hydrolysis products or organic network-forming modifiers, reactive polymeric modifiers, or reactive polymerizable modifiers. The hydrolysis products of these modifiers, when polymerized, are believed to form organic networks that are covalently bonded to the inorganic network via Si-C bonds.

Organic network-forming modifiers are (substituted alkyl) alkoxy silane compounds that are substituted with groups capable of participating in polymerization reactions with other like-substituted (substituted alkyl) alkoxy silane compounds.

Suitable network-forming modifiers include those having the formula $(R^4)_n(R^2O)_{4-n}Si$, wherein n is 1, 2 or 3 and OR^2 is an alkoxy moiety, suitable examples of which are ethoxy and methoxy. R can be a substituted alkyl moiety or aryl moiety, such as an alkacryloxyalkyl-, an acryloxyalkyl-, a vinyl, or an (epoxy-substituted) alkylsilane.

The hydrolyzed core or cladding composition can include from about 0 to about 95 mole %, preferably from about 0 to about 50 mole % of a

14
hydrolysis product of an organic network-forming modifier, such as the hydrolysis product of methacryloxypropyltriethoxysilane. When used to impart functional character, such as the permit photocuring, the hydrolysis products of organic network-forming modifiers are preferably present in an amount of from about 20 to about 50 mole %.

Where organic network-forming modifiers are employed, it can be particularly advantageous to include a photoinitiator in the hydrolyzed core or cladding composition. Suitable photoinitiators include titanocene radical photoinitiators, such as IRGACURE™ 784 or cationic ferrocenium photoinitiators, such as IRGACURE™ 261 (both available from Ciba Geigy, Ardsley, NY). The photoinitiators, where employed, are preferably included in the hydrolyzed core or cladding composition in amounts less than about 0.8 weight percent, preferably about 0.2 to about 0.8 weight percent.

Reactive polymeric modifiers are inorganic or organic polymers which are capable of participating in condensation reactions with hydrolyzed tetraalkoxysilanes, alkyltrialkoxysilanes, or aryltrialkoxysilanes.

Suitable reactive polymeric modifiers include those having the formula $(R^2O)_3O-Si-O-(P)_n-Si-O(OR^2)_3$, or $(HO)-(P)_n-OH$, where $(P)_n$ represents an organic polymer, such as polytetramethylene oxide, and OR^2 is an alkoxy moiety, such as ethoxy and methoxy.

Other suitable reactive polymeric modifiers include polydialkylsiloxanes having the formula $R^5O-[Si(R^6)_2-O]_nR^5$, wherein n is an

15

integer from about 2 to about 50, R^5 is a hydrogen, or an alkyl or aryl moiety, R^6 is an alkyl group, preferably a methyl group. Preferably, the reactive polymeric modifier is a polydimethylsiloxane having a molecular weight of from about 200 to about 900 g/mole, preferably about 550 g/mole.

The hydrolyzed core or cladding composition can include from about 0 to about 40 mole %, preferably from about 4 to about 8 mole% of the hydrolysis product of a reactive polymeric modifier.

Reactive polymerizable modifiers are substituted alkylalkoxysilane compounds which can form organic networks only in combination with a second polymerizable component which is reactive with the substituent on the substituted alkylalkoxysilane compound. The second polymerizable component may or may not be bonded to an alkoxysilane.

Reactive polymerizable modifiers include (aminoalkyl) alkoxysilanes, (aminoaryl) alkoxysilanes, (epoxy-substituted alkyl) alkoxysilanes, (epoxy-substituted aryl) alkoxysilanes, and combinations thereof.

In cases where the reactive polymerizable modifier is an (aminoalkyl) alkoxysilane or an (aminoaryl) alkoxysilane, the hydrolyzed core or cladding composition can further include a hydrolysis product of an (epoxy-substituted alkyl) alkoxysilane. Alternatively or additionally, the hydrolyzed core or cladding composition can further include an organic component having two or more functional groups reactive with epoxy groups, such as amine groups, connected via an organic backbone. Suitable backbones include alkylene moieties, and polymers diradicals.

16

In cases where the reactive polymerizable modifier contains an (aminoalkyl) alkoxysilane, the hydrolyzed bonding composition can further include an organic component having two or more functional groups that are reactive with amines, forming covalent bonds therewith.

5 The hydrolyzed core or cladding composition can include from about 0 to about 95 mole%, preferably from about 0 to about 50 mole% of the hydrolysis product of the reactive polymerizable modifier. When used to impart functional character, such as to allow photocuring or increase the plasticity of the extended silicon-oxide matrix, the hydrolysis product of the reactive polymerizable modifier is preferably present in an amount of from about 20 to about 50 mole%. In a preferred embodiment, at least one of these reactive polymerizable modifiers contains a hydrolytically stable silicon-carbon bond.

15 Non-interacting interpenetrating network modifiers are organic polymers, preferably organic polymers, which do not contain groups capable of forming Si-C bonds with silicon atoms, or precursors to such organic polymers which are capable of forming such organic polymers by, for example, radical polymerization.

20 These non-interacting interpenetrating network modifiers can be incorporated into the hydrolyzed core or cladding composition in amounts of from about 0 to about 50 mole %. When used to impart functional character, such as to increase plasticity or to introduce photoactive polymers into the extended silicon-oxide matrix, the non-interactive interpenetrating network modifiers are preferably present in an amount of

from about 5 to about 25 mole%. Further details with respect to these non-interacting interpenetrating network modifiers can be found, for example, in U.S. Patent No. 5,412,016 to Sharp, which is hereby incorporated by reference.

Where increased indices of refraction of the polymerized hydrolyzed core or cladding composition are desired, the composition can further include one or more reactive compounds containing an element selected from the group consisting of Ge, Ti, Zr, Hf, Er, Nd. The alkoxides can, optionally, be hydrolyzed to their hydrolysis products.

The amount of alkoxide and the hydrolysis products thereof collectively present in the hydrolyzed core or cladding composition depends on the refractive index desired upon polymerization. Suitable amounts of alkoxide and hydrolysis products thereof collectively present in the hydrolyzed core or cladding composition range from about 0 to about 25 mole%, preferably from about 0 to about 15 mole%, depending on the desired change in the index of refraction and stability of the hydrolyzed core or cladding composition.

The refractive index of the polymerized hydrolyzed core or cladding composition is preferably varied by incorporating aryltrialkoxysilanes (particularly phenyltrialkoxysilanes), and/or aryltrifluorosilanes (particularly phenyltrifluorosilanes) into the hydrolyzed bonding composition.

The hydrolyzed core or cladding composition preferably contains a fluoride source, such as a hydrolysis product of a fluorosilane, examples of which include alkylfluorosilanes. Other suitable fluoride sources, such as

hydrogen fluoride, ammonium bifluoride and other fluoride salts which dissociate may be used. The incorporation of a fluoride source is advantageous where suppression of the ca. 3300 cm^{-1} SiO-H infrared absorption band is desired. Such a case is where the optically transmissive materials must pass infrared radiation without significant attenuation.

The amount of fluoride source present in the hydrolyzed core or cladding composition depends primarily on the acceptable level of infrared absorption. Where the fluoride source is the hydrolysis product of a fluorosilane, significant reduction of the Si-OH absorption band can be achieved when the amount of the hydrolysis product of the fluorosilane ranges from about 0 to about 25%, preferably from about 5 to about 15 mole%.

Particularly preferred core or cladding layer compositions for use in the practice of the present invention are polymerizable inorganic-organic hybrids which include a silane selected from the group consisting of a tetraalkoxysilane, an alkyltrialkoxysilane, an aryltrialkoxysilane, a trialkoxysilane, an alkacryloxypropyltrialkoxysilane and combinations thereof, in a total amount from about 50 to about 95 mole%. The polymerizable inventive composition also includes a network modifier selected from the group consisting of a monomeric dialkyldialkoxysilane and a polymeric polydialkylsilane in an amount of from about 4 to about 25 mole%, an aryltrifluorosilane in an amount of from about 5 to about 20 mole%, a tetraalkoxytitanium in an amount of from about 0 to about 10

19
mole% and a tetraalkoxygermanium in an amount of from about 0 to about 20 mole% of the sol-gel composition.

Hydrolyzed core or cladding compositions can be prepared by adding water to core or cladding layer precursor materials which contain an alkoxysilane. Hydrolysis begins immediately upon the addition of water, and results in the replacement of alkoxy groups with hydroxy groups. The rates of hydrolysis of the various silanes can differ, depending on the nature of the substituents bonded to the silicon atoms. Therefore, it can be advantageous to begin the hydrolysis process of various alkoxysilanes (or alkoxides of other elements, such and tetraethoxygermanium) separately and mix them together after some or all of the alkoxy groups have been hydrolyzed.

The amount of water used in carrying out the hydrolysis phase of the curing process can vary widely, such as from about 25% to about 800% of the stoichiometric amount required to completely hydrolyze all of the alkoxy-silicon bonds present in the precursor materials based upon the reaction $2\text{--SiOR} + \text{H}_2\text{O} \rightarrow \text{--Si-O-Si--} + \text{ROH}$. Preferably, the amount of water added is from about 75% to about 100% of the stoichiometric amount. As little as 25% of the stoichiometric amount may be added and/or water may be added in stages to the gel.

Hydrolysis reactions of alkoxides liberate alcohol as a reaction product. Alcohols are removed from hydrolyzed core or clad compositions by opening the vessel to air and evaporating. The hydrolyzed core or clad composition becomes increasingly viscous as alcohol is removed.

Hydrolysis can be carried out using the following general procedure.

A core or cladding layer material, including a selected alkoxy silane, together with one or more of the optional additive modifiers, is dissolved in a suitable solvent. Preferably, the solvent is non-reactive with, and capable of, solubilizing all of the precursor composition. The preferred solvent is ethanol. Where reaction rates of the precursors are sufficiently similar, the precursor composition may be mixed and hydrolyzed directly, without a solvent.

Water and acid are added to the solution of the precursor composition, preferably at reflux. The water and acid are first mixed in a solvent, which may be the same solvent used to dissolve the precursor composition. The acid and water can be added at once, slowly, either dropwise or in several Aliquots. The addition is carried out over the course of 20 minutes to 8 hours, preferably 1 to 3 hours, preferably, while maintaining the reaction mixture at reflux and with stirring. After the addition is complete, the reaction mixture may be stirred at reflux for an additional period of time, preferably about 30 minutes. To precisely control the amount of water introduced into the reaction mixture, the addition and optional subsequent stirring and refluxing can be carried out in an inert atmosphere, such as nitrogen or argon. When reactions are conducted with no added solvent, the water is added in one or two aliquots, and mixed vigorously at temperatures from about 50 to about 90°C, until homogeneous.

21

Hydrolyzed core or cladding layer compositions containing primarily alkyl trialkoxides can be advantageously prepared by the following alternate general method. A core or cladding layer composition precursor material, including a selected alkoxysilane, together with one or more of the optional modifiers, is prepared without the addition of solvent. Water in the desired amount is added to the composition precursor material. The addition of water can be carried out at room temperature; or the composition can be heated, such as in a hot water bath. Preferably, the core or cladding layer composition precursor material, prior to addition of water, is at a temperature from about 60°C to about 30°C. Alternatively, water may be added at a reduced temperature to improve homogeneity via slow hydrolysis. The amount of water with which the precursor material reacts is better controlled if the addition is conducted under conditions which exclude moisture in the ambient air, such as by capping the reaction vessel. Addition of water to the precursor material frequently produces a phase separated mixture. In these circumstances, the phase separated mixture can be agitated to dissolve the water in the precursor material. Agitation is preferably carried out in a vessel isolated from the ambient atmosphere, such as with a cap. After agitation, the system is preferably vented (if capped) and then rested, preferably isolated from the ambient atmosphere, at a temperature from room temperature up to about 100°C for a period of time from about 15 minutes to about 1 hour. After cooling, the hydrolyzed core or cladding composition can, optionally, be aged, preferably at room temperature and for from about 1 to about 10 days.

Both germanium and titanium alkoxydes hydrolyze rapidly. It is desirable, therefore, to delay their addition to the precursor material until the alkoxy silanes are at least partially hydrolyzed. The delay incorporates the germanium and titanium more uniformly into the inorganic matrix.

5 The hydrolysis reaction may be catalyzed by a mineral acid or an organic acid, preferably HCl. The amount of acid used in the hydration reaction can be from about 0 to about 5%, expressed in terms of equivalents of acid per mole of water used. When the precursor material contains a fluoride source, such as PTFS, the use of acid provides little
10 advantage.

The amount of water used in the hydrolysis reaction can be from about 10% to about 200%, expressed in terms of moles of water per moles of hydrolyzable alkoxy group. The stoichiometric hydrolysis of one mole of alkoxy group requires 0.5 moles of water. In cases where a
15 polydialkylsiloxane is contained in the precursor material, the amount of water is preferably from about 45% to about 55%.

After acid and water addition and optional additional reflux, the resulting hydrolyzed core or cladding composition can be stored at room temperature for from about 3 to about 30 days before use in connecting
20 optically transmissive components. Shelf life can frequently be extended by employing dimethylformamide as the reaction solvent, or as a cosolvent with an alcohol.

In cases where the hydrolyzed core or cladding composition contains germanium or titanium, its shelf life can be extended by adding

the germanium or titanium alkoxide²³ to the sol after hydrolysis of the alkoxy silanes is partially, or preferably, totally completed. Shelf life can also be extended by reducing the amount of water employed in the hydrolysis process, such as from about 50% to about 25% of the stoichiometric amount.

The core or cladding layer composition is applied to a substrate to form a layer. As is discussed in detail below, the layer may be patterned using a mold. The core or cladding composition is then polymerized to form the planar waveguide device. It is often beneficial to allow the reaction by-product alcohol(s) to evaporate from the core or cladding composition prior to polymeric action. Polymerization, as used in this context, refers to polymerization of the inorganic component of the hydrolyzed core or cladding composition. Polymerization can be effected at room temperature over a prolonged period of time. However, it is usually desirable to accelerate the polymerization process, such as by application of thermal radiation. Heat can be applied from any conventional thermal radiation source, such as a flame, a heat gun, a high temperature oil bath, or radiation, such as with a focussed infrared laser. The amount of heat applied is preferably sufficient to polymerize the hydrolyzed core or cladding composition quickly but without causing significant trapping of solvent as bubbles. The temperature for polymerization is about 150°C. to about 300°C., preferably 225°C. to about 250°C. The polymerized composition is sufficiently strong to withstand normal handling.

24

In some instances, the optical and thermal properties of the polymerized core or cladding composition can be improved by condensing the polymerized core or cladding composition. Preferably, the polymerized bonding composition is exposed to a temperature greater than that used to effect polymerization.

Upon polymerization, the core or cladding formed depends upon the components of the initial core or cladding composition. Compositions, which contain hydrolysis products of one or more modifiers, form core or cladding layers containing a silicon oxide matrix (i.e., Si-O-Si network), in which a portion of the silicon atoms are directly bonded to substituted or unsubstituted hydrocarbon moieties.

Where the core or cladding composition contains a hydrolysis product of an inert network modifier, or a polydialkylsiloxane, the hydrocarbon moieties are unsubstituted alkyl or aryl moieties. Where the core or cladding composition contains a hydrolysis product of an active network modifier, the hydrocarbon moieties are substituted alkyl or aryl moieties. Where the core or cladding composition contains a hydrolysis product of an organic network-forming modifier, the hydrolyzed moieties are substituted alkyl or aryl moieties, such as alkylene or arylene moieties. The alkylene or arylene moieties are bonded on either end to silicon atoms of the extended silicon-oxide matrix. This forms Si-R-R'-R-Si bonds where R is an alkylene moiety, and R' represents the radical polymerization product of the polymerizable organic functional groups contained in the modifier.

Where the hydrolyzed core or cladding composition contains a hydrolysis product of a reactive polymerizable modifier other than a polydialkylsiloxane the hydrocarbon moieties are substituted alkyl or aryl moieties, such as those containing alkylene or arylene moieties having the formula -R-. The alkylene or arylene moieties are bonded on either end of silicon atoms to form Si-R-Si bonds wherein R represent an organic polymer diradical.

Where the hydrolyzed core or cladding composition contains a hydrolysis product of a reactive polymerizable modifier, the hydrocarbon moieties are substituted alkyl or aryl moieties, such as those containing alkylene or arylene moieties having the formula -R-R'-R-. The alkylene or arylene moieties are bonded on either end of silicon atoms to form Si-R-R'-R-Si bonds wherein R is an alkylene moiety, and R' contains a moiety produced by a reaction of an amine with an amine-reactive functional group.

The fraction of silicon atoms directly bonded to substituted or unsubstituted alkyl moieties can be from about 4% to about 100%, preferably from about 20% to about 100%, most preferably from about 50% to about 100%.

Hydrolyzed core or cladding compositions which contain non-interacting interpenetrating network modifiers or their hydrolysis products form bonding materials containing an extended silicon oxide matrix (i.e., a Si-O-Si network) and an interpenetrating organic polymeric matrix. The extended silicon-oxide matrix and interpenetrating organic polymeric matrix

26

are not bonded to one another so that substantially none of the atoms in the interpenetrating organic polymeric matrix are bonded atoms in the extended silicon-oxide matrix.

A common problem with sol-gel processed materials is structural damage incurred during the polymerization and curing as a result of mass loss and condensation. The core and clad compositions possesses unique visco-elastic properties during the polymerization and curing processes that enable them to avoid severe stress build-up. In a preferred embodiment, the hydrolyzed core or clad composition may be air dried to remove alcohol reaction by products, and any solvent used in the hydrolysis step. The drying affords a viscous clear fluid whose mass is between 40% and 50% of the original mass of the hydrolyzed core or clad composition sample. The dried hydrolyzed core or clad composition may be heated to temperatures as high as 100°C with additional mass loss of 2 to 5% of the original hydrolyzed core or clad sample. Reheated material retains the ability to be plastically deformed without permanent damage. The dried core or clad composition may be cured at temperatures of 220 to 260°C with mass loss of 2 to 5% of the original sample, resulting in an elastic form of the material.

27

The following table sets out mass loss experienced by a preferred embodiment of the inventive composition.

Mass Loss Table

Step	Precursors	Hydrolyzed sol	Dried Sol	Partially cured gel	Cured gel
Form	Fluid liquid	Fluid liquid	Viscous liquid	Plastic solid	Elastic solid
% original mass	100	100	45 (room temp.)	43 ($< 100^{\circ} \text{C}$)	41 (250°C)

Note that at least 50% of the mass loss occurred during the liquid and plastic states, prior to the plastic/solid state. Because less than 6%, and preferably no more than 4%, of the original mass is lost in a solid state, the cracking problems of prior sol-gels are avoided.

For application in conventional optical fiber networks, the ideal index of refraction would be about 1.4565 for cladding layers and 1.465 for waveguide cores at 632 nm. Compositional effects, such as inclusion of methyl modifiers, or structural effects, such as porosity in the material, can significantly lower index of refraction. Other compositional effects such as the inclusion of phenyl modifiers or incorporating germania or titania can significantly increase the index of refraction. Preferably, the waveguide core index of refraction falls within the range of 1.4-1.55 and the cladding index of refraction falls within the range of 1.3-1.6.

The index of refraction may be preferentially varied by incorporating phenyltrialkoxysilane, phenyltrifluorosilane, or combinations thereof into

the composition. Compositions containing 0.04 moles of silicon and containing components having phenyl groups bound directly to silicon atoms may be prepared. The index of refraction at 588 nm was measured by comparison with a series of standard index of refraction oils using the Becke line method. The table below details the silicon relationship of the various compositions and therein indices of refraction. The index of refraction data for these compositions shows the capability of tuning the index of refraction to a desired value between 1.39 and 1.55.

Si-C6H5/(Total Si)	Index of Refraction
0	1.39
9	1.43
27	1.47
80	1.55

The foregoing discussion discloses a core composition precursor material and a cladding composition precursor material. Also discussed is how to process the precursor material for cladding composition or core composition.

C. Specific Examples of Materials

Used to Form Planar Optical Waveguide Devices

The invention is further described in connection with the following specific examples.

One suitable material for this invention is a sol-gel based silsesquioxane. The material is made from a multicomponent mixture of alkyl- and arylalkoxysilanes, fluoride, and water.

C.1 Synthetic Preparation I

The following describes a process for forming a core or cladding composition starting from a core or cladding composition precursor material.

The preparation is based on a 0.03 moles of silicon formulation with 8 mole % equivalent PDMS (polydimethylsiloxane), 73% MTES (methyltriethoxysilane) and 19% PTES (phenyltriethoxysilane). This will provide a material with an index of refraction of about 1.4565 at 632 nm (clad formulation). The composition for a core index (1.465) is given in {brackets}.

Volumes

1)	PDMS	0.18cc	
2)	MTES	4.36cc	{3.95cc}
3)	PTES	1.40cc	{1.88cc}
4)	HF (48%wt)	0.28cc	
5)	H2O	0.55cc	

HF and PTES are mixed together in a closed nalgene vessel. The mixture is then heated in a 75°C water bath for 15 to 30 minutes. This step pre-hydrolyzes and fluoridates the PTES component of the mixture. MTES and PDMS are then added to the mixture and heated for an additional 15 to 30 minutes. Finally, the water is added. Approximately 1

to 3 minutes of stirring are required to homogenize the solution after water addition. The sol-gel hybrid is aged for 3 to 6 hours at 75°C.

The sol should be clear with low viscosity after cooling. The sol in this state is suitable for forming a thin coating. Thus, the sol forms a cladding composition or a waveguide core composition material. After firing, the films look very transparent and flaw free under the microscope.

The sol can be dried to an ethanol free "dried" form by pouring out a sol and allowing the ethanol to evaporate. This form of the material is suitable for transfer molding applications to form waveguide cores. To dry the sol, 1 gram of sol is placed into a 10cc Pyrex beaker with 2.5 cm diameter. One gram of sol will dry to about 0.39 grams of dried sol. The dried sol will reduce to 0.34g after heating to 240°C. The most appropriate heating schedule for process both films and monoliths is to ramp at 1°C per minute to 240°C, hold for 10 minutes, and then cool at 1 to 2°C per minute. The slow rate may not be required, but is convenient for overnight firings. The disks are clear and colorless.

C.2 Synthetic Preparation II

The following describes an alternate process and formulation for forming a core or cladding composition.

The following formulation eliminates the PDMS and uses diphenyl dimethoxysilane in its place. The formulation provides longer shelf life but it has a greater propensity for cracking during firing in either thin film form or in making monoliths.

Volumes

6)	MTES	5.14cc	{4.78}
7)	DPDMS	0.545cc	(diphenyldimethoxysilane)
8)	PTES	0.435cc	{0.87cc}
9)	HF (48%wt)	0.28cc	
10)	H2O	0.55cc	

The preparation is similar to Synthetic Preparation I discussed above: HF is added to the mixture of PTES and DPDMS, and allowed to react for 30 minutes at 75°C. MTES is then added, and heated for 30 minutes longer. The water is finally added, and shaken until clear. Age for 3 hours at 75°C. This material handles similarly to the first formulation, except that the masses retained from 1 gram of sol are 45% on drying and 38% on curing to 250°C. Films and gels with this formulation are transparent during drying and curing, and are colorless when viewed through the edge. A near infrared absorption spectrum of a 1mm disk of this material is provided in Fig. 7.

C.3 Synthetic Preparation III

The following describes another alternate process and formulation of forming a core or cladding composition. This method employs phenyltrifluorosilane as the fluoride source rather than HF. Inorganic-organic hybrid materials made with this preparative method are suitable for forming highly transparent and crackfree monoliths and films. The

formulations are given for a clad composition and a core composition in { }.

	Volumes,cc	Clad	{Core}
11)	PDMS	0.18	{0.18}
12)	MTES	4.27	{3.89}
13)	PTES	0.84	{1.30}
14)	PTFS	0.365	{0.365}
15)	H2O	0.745	{0.745}

10 Mix together the PDMS, MTES, PTES, and PTFS, in a capped polypropylene, or Nalgene container. Heat the mixture to 75°C in a hot water bath for 5 minutes to homogenize. Add H₂O to the warm mixture and recap. The mixture phase separates initially. Heat to 75°C and shake vigorously until the solution is clear, usually about 20 minutes. Allow the
15 system to react for three hours before cooling. The composition should be clear and fluid.

The material handles similarly to the first formulation. The mass retained on drying is about 45% and after curing at 250°C the retained mass is 40% of the original sample. 1 mm thick discs were made by
20 drying and curing a sample in a cylindrical mold. Near infrared absorbance spectra for a clad sample are given in Figs. 5 and 6.

The above described sol liquid compositions (synthetic preparation I and synthetic preparation II) are used as composites for cladding layers and patterned core layers in planar waveguide devices. The following

sections describe the process for forming the cladding and patterned core layers.

D. Process for Forming Planar Optical Waveguide Device

Two distinct process steps are required for the formation of planar waveguides, deposition of continuous thin films for clad layers, and deposition of patterned thin films for core layers. These will be described independently.

To avoid the introduction of flaws, coating processes should, in general, be conducted in low particulate environments. The sols are prepared in a standard lab environment, and then are brought into clean room conditions. Substrates are cleaned and dried in the clean room. The sols are passed through 0.2 micron filters before application as coatings to remove any particulate matter. All drying should preferably be conducted in the clean room, and firing should be done either in the clean room or by techniques that minimize introduction of particles to the surface in a standard lab environment.

D.1 Clad Layers

Two basic techniques may be required. A uniform clad layer may be needed to support a core layer if a substrate is not able to function as a clad layer in the designed planar waveguide device. When a clad layer is to coat a patterned core array, it is necessary to fill regions that could

form traps for bubbles, especially features like Y-junctions, or slab to ridge waveguide junctions. Each of these coating techniques are addressed here.

To make a film of sol liquid (cladding composition) of discrete thickness, any of a number of liquid phase deposition methods may be employed. A cleaned substrate may be dipped into the sol-gel and withdrawn at a fixed rate of speed to generate a coating. The coating thickness is proportional to the withdrawal speed. A sol liquid film may be spun onto a flat surface, by first saturating the surface to be coated with the sol liquid, and then spinning at a rate of 1000 to 4000 RPM. The thickness is inversely proportional to the spinning speed. A film may be prepared by simply draining excess sol from a saturated surface.

The most successful method for overcoating a patterned ridge array of waveguide cores is to drop the fluid sol onto the ridge waveguide array and allow the sol to wet the region between the ridges. This is especially important when the array includes Y branch elements, because to rapidly dip or spin coat these features, bubbles can be trapped in the closed regions. Once the entire surface is well wetted, and all features are filled in, a spin or drain coating technique may be employed to provide a sufficient thickness. In these cases, the surface is saturated with sol, and is then drained or spun to provide sufficient material coating. It is also possible to simply provide the appropriate volume of sol to the substrate to provide a sufficient final coating thickness, and allow gravitational spreading to give the needed thickness uniformity. The greatest barrier to

35

this simple method is that evaporation of alcohol, a reaction by-product, causes the viscosity to increase rather rapidly, so coating a large sample in this way becomes difficult. By any of the above techniques, the final film is processed with drying and thermal treatments to give the final silsequioxane compositions. The film is allowed to air dry for 15 minutes to an hour at temperatures between 20 and 45°C. Then the sample is transported to an oven and cured. The preferred curing schedule is to ramp the temperature from 25 to 240°C at 4°C/minute; hold for 60 minutes and then to ramp to 25°C at 4°C per minute.

Several key material and process attributes enable the application of advantageous overclad layers. The compositions have low intrinsic optical loss. The ability to control the index of refraction enables design flexibility. The ability to coat a thick film with a low viscosity sol (cladding layer composition), and then convert that film to a 40 micron thick solid film without cracking or large residual stresses is also important. This is a significant problem in classical fully inorganic sol-gel techniques where cracking is prevalent when film thickness exceeds about 1 micron. The compositions described show excellent environmental durability.

D.2 Patterned Core Layers

In accordance with an illustrative embodiment of the invention, arrays of waveguide cores may be formed using either a transfer printing technique or an embossing technique. The objective is to achieve a high resolution pattern with a high index core composition that takes advantage

36

of the unique attributes of the sol-gel compositions to produce waveguide arrays rapidly with low processing cost. Two methods will be described generally. These techniques replace the prior art lithographic techniques for forming arrays of waveguide cores.

Both of the approaches (printing and embossing) take advantage of the ability to dry the sol liquid gel composition to a viscous form. The viscous material can be doctor bladed or rolled into a mold such as an intaglio imaging plate or can be embossed by a mold to enable the formation of the pattern. Thermal curing can then set the structure before the material is released from the mold.

As shown in Figs. 3A, 3B, 3C, 3D, and 3E in the first of the approaches, the desired pattern 32 is provided in negative relief on a negative master film 30 which is compressible to conform to the substrate region to form a "foot" or compressed region (Step A). The negative master film 30 is a film where the core pattern is depressed on the surface of the film and may be formed by the following process. A desired waveguide pattern is etched into a silica disc (not shown). The disc is then coated with an appropriate material that can be separated from the silica disc with complete replication of the pattern to form the negative master film 30. Further, the selected material should have good release properties with the inventive materials of the present invention. Nickel is one material that provides both the ability to separate from the silica patterned surface and the ability to provide a good release surface for inventive materials. The nickel can be deposited onto the silica plate by

electroless deposition, or other known methods. The nickel film is then peeled from the silica plate to form the negative master 30. Preferably, the negative nickel master 30 is mounted on a flexible backer 33, such as an elastomer. The dried sol material 34 is loaded into the relief channels 32 in the nickel master 30. This may be done using, for example, a doctor blade 35 or preferably a roller applicator. Excess sol is removed from the surface (Step A). The doctoring works well to force the sol into the pattern and to scrape the excess off. A roller works well in that it results in a positive meniscus, which aids in contact and attachment to the substrate. The inventive material is then cured to a point where it can retain its shape, and still adhere to the substrate 36 of the planar optical device to be formed. The substrate 36 is brought into contact with the nickel master 30, simultaneously making contact with the inventive material 34 in the channels 32. The compressible nickel master 30 preferably contacts the substrate 36 only at a single "foot" 37 location at a time by rolling the master across the surface. Preferably, the sol-gel is compressed against the substrate 36 and simultaneously cured using, for example, a heat or radiation source 38. As the nickel master 30 separates from the substrate 36, and the inventive material 34 is released from the nickel master 30 and adheres to the substrate surface replicating in positive relief the waveguide array (Step C). An overclad layer 39 is deposited and the material is then finally cured to a temperature of 240°C (Step D).

Figs. 3F and 3G show a variation of the approach illustrated in Figs. 3A, 3B, 3C, 3D, and 3E. First, a second plate 31 is pre-coated with overcladding material 39. A positive master film 30 in which the core pattern is raised on the surface of the master is in contact with the second plate 31. When the master film 30 rolls across the overcladding material 39, depressions are formed in the overcladding material 39 through contact with the desired pattern 32 in the positive master film 30. The overcladding material 39 is also preferably simultaneously cured with a curing device 38, such as a heat or radiation source (Step A). Next, the dried sol material 34 is loaded into the depressions using, for example, a doctor blade 35. The sol material may be partially cured with the curing device 38 (Step B). Preferably, the cladding material and the sol-gel material are simultaneously cured by focused radiation or localized heat while in contact. Next, the combination of the sol material 34 and outer cladding material 39 contacts undercladding 39' on the substrate 36 and are preferably simultaneously cured with a curing device 38 (Step C). As a result, the core is deposited on the substrate already embedded in the overcladding 39. As discussed above, it may be desirable to put an undercladding layer 39' on the substrate 36 prior to depositing the sol material 34 and overcladding 39.

Figs. 3H and 3I show another variation of the approach illustrated in Figs. 3A, 3B, 3C, 3D, and 3E. A second plate 31 is pre-coated with overcladding material 39 (Step A). Next, the dried sol material 34 is loaded into a relief pattern 32 in a negative master film 30 using, for

39

example, a doctor blade 35. The sol material may be partially cured with the curing device 38. The sol material then contacts the overcladding material 39 on the second plate 31 and adheres to the outer cladding material (Step B). Preferably, the cladding material and the inventive material in the channels of the negative master 30 are simultaneously cured by focused radiation or localized heat while in contact. Upon separation of the second plate 31 from the negative master 30, the inventive material in the channels remains adhered to the overcladding 39 on the surface of the second plate 31, forming a raised pattern of core material thereon. Then this pattern may be further overcoated by an additional layer of overcladding 39''. This can either be a continuous overcoat or be overcladding deposited or printed between the raised pattern by typographic printing, microdispensing, ink jet printing or the like. In the non-continuous case, the deposited material should exhibit a positive meniscus adjacent to the embossed (raised) pattern in order to completely envelop the core material upon transfer to the substrate.

Next, the combination of the sol material 34 and overcladding material 39 contacts the substrate 36 and preferably simultaneously cured with a curing device 38 (Step C). As a result, the core is deposited on the substrate already embedded in the overcladding 39. As discussed above, it may be desirable to put an undercladding 39' on the substrate 36 prior to depositing the sol material 34 and overcladding 39. When this is done, it may obviate the need for the second application of the overcladding 39'' on plate 31.

40

In a preferred embodiment of the invention, the material changes state from a liquid to solid when under compression (i.e., while in contact with the substrate). Cohesion of the material onto the substrate causes the material to remain on the substrate while the compressible master separates from the substrate. The state change may be attained by heat or radiation (light), which may be focused on the compressed area (the "foot") or, in the case of heat, by heating the substrate. It is possible, but less desirable, to use cooling or drying to obtain the change of state.

A number of variations on the technique may be important to consider for optimization of the replication of the pattern and to minimize cost. The surface to which the negative master foil is attached may be flat or curved as in a drum. A curved surface has many advantages in scale up, where the drum can be loaded with sol-gel material, doctored, heated and applied in a continuous process. One advantage is avoiding air entrapment. The release of the gel from the negative master to the substrate will occur along a single front rather than over the full area of the pattern, which will lower stresses and most likely reduce flaws. The curing conditions are another set of process variables. The thermal treatment can occur in discrete steps, or can be introduced as part of either the doctoring or transferring step of the process. The nickel master can be heated, with transfer to a cool substrate, or the master can remain cool and the substrate can be heated so that the transfer and cure be accomplished on contact with the substrate. The release from the master can also be enhanced by release agents. The substrate may be coated

with cladding material to facilitate transfer and the overcladding 39 added to embed the cores 34 in cladding.

In the second of the approaches, an embossing technique is employed to provide the desired waveguide array pattern. This approach is illustrated in Figs. 4A, 4B, 4C, 4D, and 4E. As shown in Figs. 4A, 4B, 4C, 4D, and 4E, the embossing element 42 embodies a positive relief structure 44 of the waveguide core array. That is, the embossing element is a positive master in which the core pattern is raised on the surface of the element. As shown in Step A, the substrate 40 is coated with a sol-gel low index clad layer 41 of depth greater than the maximum depth of the waveguide core array. The clad layer 41 is partially cured to a point where the viscous flow would still allow deformation without cracking or it is heated so it softens to create viscous flow and then it is cooled instantly. The embossing element 42 is pressed onto the clad layer 41. Heat is applied to cure the film to an elastic state (Step B). The embossing element 42 is then lifted to provide a negative relief pattern 46 in the clad layer 41 (Step C). To complete the structure, a high index waveguide core composition 48 is then doctored into the negative relief regions 46 of the clad 41 and is itself cured (Step D). Finally, a clad layer 50 is deposited onto the core filled clad layer 41 to provide the channel waveguide structure (Step E).

A number of variations on the technique may be important to consider for optimization of the replication of the pattern and to minimize cost. The embossing element should release from the clad layer in order

to minimize defects arising from adhesive pullout. Preferably, the embossing element is formed with a surface quality and roughness equal to the glass surface on which it is being deposited. Nickel would be a good material for the same reasons that were indicated in the intaglio printing process. Silica would require release agents. It would be desirable to mount the embossing element on a curved element, such as a drum, so that the point of release is a compressed "foot" region rather than a two dimensional area so that lower release stresses would be experienced. The curing could be accomplished in discrete process steps. Alternatively, the cure step from plastic to elastic states could be accomplished by heating the embossing element and imparting both the form and the energy needed to cure in one step.

The exact degree to which a first sol-gel layer should be cured before the next sol-gel layer is applied may be variable in some cases. The final cure could then effectively cure all three layers.

While the compositions and processes described so far use only thermal curing processes for conversion of the sol-gel material from plastic to elastic states, additives to the formulations could enable photocuring with UV or visible light radiation. In this case, light may be transmitted through the substrate into the compressed region. In any event, if light is used for curing at least either one of the film or the substrate should be made of a material which is transparent to light. Preferred substances include fused silica, soda-lime, borosilicate glass, or a fluorocarbon polymer such as FEP (fluorinated ethylenepropylene).

43

The methods described above permit forming structures having a resolution (i.e., a width of a core may be) less than 1.0 micron, and preferably less than 0.6 microns.

E. Examples of Planar Optical Waveguide Devices

In combination, a complete planar waveguide structure can be made, or if desired, an overclad layer may be provided on a conventionally etched silicate core waveguide array. The primary advantage that can be realized from this invention is cost. The use of the inventive overclad on conventionally patterned glass waveguide core arrays can provide advantages. The low process temperature used avoids any deformation on etched core ridge waveguides, whereas high temperature processing can distort the original waveguide shape. The low temperature and low modulus of the inventive overclad also results in low stress fields on the ridge waveguides, so that stress induced polarization effects can be minimized.

E.1 Overclad Example

An array of straight waveguides was overclad to measure loss and overclad coating characteristics. A silica wafer was coated with a glass core layer by flame hydrolysis methods, and was patterned by photolithographic and reactive ion etch methods. A chip (2 cm x 2 cm) was cut from a 10 cm diameter wafer which had an array of straight waveguides. A sol liquid composition according to the present invention

44

was prepared with a target index of 1.455 at 632 nm. In a clean room, the sol was filtered through a 0.2 micron filter to remove large particulate matter. The fluid sol was placed dropwise onto the waveguide array, first wetting the length of the ridge waveguides, and then saturating the entire surface of the chip. The sample was tipped and an absorbent towel was used to wick away excess material. The coated chip was then placed flat and allowed to dry for about an hour. The sample was then placed in a 100°C oven for one hour. The sample was then transferred in a covered container from the clean room to an oven outside the clean room. The thermal process was completed by firing to 240°C at 1°C per minute holding for 10 minutes, and then cooling at 1°C per minute. Losses at a wavelength of 1550nm measured for this sample were approximately 0.5 db per cm and beneficial transmission characteristics were measured at the optical telecommunications windows within 1200-1600nm.

E.2 Patterned Core Example

A laboratory sample process for making a patterned core is described. A nickel negative master was prepared by electroplating a foil onto a silica wafer that had been previously reactive ion etched (RIE) to provide straight waveguides and 1 x 8 splitters. The foil (approximately 0.004" (4 ml) thick) was peeled from the silica master and mounted onto a flat silica wafer with double stick tape. The resulting nickel surface was flat only over limited regions of the specimen. A sol was prepared and was allowed to dry to provide a viscous fluid. A drop of material was

45

placed onto a flat region of the nickel foil and was spread into the relief pattern by means of swiping with a doctor blade. The excess material was removed from the surface with the blade leaving sol in the negative relief channels in the negative master. A 1" diameter silica disc was pressed onto the filled region of the negative master and was loaded with a 10 gram weight. The weighted sample was placed in an oven at 75°C for 12 hours, and then was additionally heated at 120°C for 1 hour. After cooling, the weight was removed. A spatula was used to pry the disc from the foil. The disc popped off the nickel surface, pulling much of the filled gel material out of the channels. The silica disc with adhered ridge waveguides was then heated to 240°C at 1°C per minute, held for 10 minutes and then cooled at 1°C per minute rate. Waveguides replicated the channel width and possessed well defined edges and unflawed surfaces showed that the sol-gel material releases well from the nickel foil.

F. Spectra of Materials Used to Form Planar Waveguide Devices

The sol-gel materials utilized in the present invention have interesting spectra. Such spectra are illustrated in Figs. 5, 6, and 7. Spectra samples of 1nm thick disks of the inventive hybrid inorganic-organic solid material comprised of methy-siloxane groups, phenyl-siloxane groups, and fluorine were analyzed according to standard visible-near IR spectrum analysis procedures. Reflection and scattering losses are taken into consideration by establishing a base line 101.

46

The attached spectra are typical for the preferred composition ranges of hybrid inorganic-organic solid materials. Fig. 5 is a spectrum showing the visible-near IR range from 300nm to 2500nm, and Fig. 6 is the boxed inset from that spectrum showing the near infrared. The telecommunications windows are centered on at 1310nm (a range from about 1270 - 1330nm) and at 1550 (a range from about 1525-1570nm), in both cases the intrinsic absorption of the inventive materials in these wavelength ranges is very low as measured from baseline 101. A band is present at 1520nm, as seen in Fig. 7, which is apparently due to a combination band of C-H and SiOH vibrations. As seen in the figures, in the ranges between 1270-1330nm and 1525-1570nm, the absorbance is very low. This baseline absorbance is due to reflection and surface scattering losses and does not represent any intrinsic absorption in the sample. With a base line at 0.195 AU, the small peak at about 1530 is approximately 0.03AU, which translates to about 0.3 dB/cm. Figs. 6 and 7 show how absorbance is further reduced by deuteration of the inventive material. In Fig. 6, peaks 102 are shifted to 202, and peak 303 is shifted to 203 by the replacement of hydrolyzer with deuterium. The calculated spectral positions of equivalent features in a fully deuterated system is provided in Fig. 7. Deuteration on methyl and phenyl groups is accomplished by synthesis of the precursors, and on the silanol by hydrolysis with D₂O. Of these deuteration processes, the easiest to practice is the hydrolysis with D₂O, because this form of water is readily available. Fig. 7 shows that a reduction in the spectral intensity of silanol

47

peak at 1380nm and the combination band at 1520 nm can be accomplished by using D₂O instead of water in the preparation. The presence of any peak intensity in these regions is due to the fact that HF was used in the synthesis along with its water (H₂O) of hydration which provides 1/3 of all the needed water for the hydrolysis reactions.

Particularly useful attributes of the described formulation are its transmissive properties at 1310nm (from 1270-1330nm) and at 1550nm (from 1525-1570nm, preferably 1530-1565nm). In general, the optical spectrum in the near IR of hybrid materials is dominated by vibrational overtones from the organic modifiers, and incompletely reacted silanol groups. The formulations according to the present invention have been carefully designed to provide a minimal number of vibrational modes so that the overtone and combination band spectrum in the near IR would be as uncomplicated as possible. In the composition, only C-H and SiO-H stretches and phenyl group bending modes are active in the near IR. The positions of the C-H stretch overtone bands are from 1530 to 1750nm and 1150 to 1200nm. The position of the silanol stretching band is from 1370 to 1410 nm. Phenyl group ring bending is active in the region from 1700 to 2000nm. Of these vibrational modes, only the silanol is not an essential part of the structure, arising from incomplete condensation of the siloxane network. The silanol content is low and minimized in these formulations by incorporation of fluoride and by the unusual ability of the material to proceed to a high degree of condensation while still in a viscous state. The importance of the low silanol content in the final

product is that undesired combination bands are minimized. Thus, the absorbance has been driven to very low values at the telecommunications optical windows at 1310nm (1270-1330nm) and at 1550nm (1525-1570nm). This makes the formulation especially useful for telecommunications applications. The inventive compositions provide particularly good transmission with low absorption in the wavelength ranges of 1200-1360nm and 1430-1620nm. The inventive compositions have particularly good transmission in the preferred ranges of 1220-1330nm, 1525-1570nm, and the more preferable range of 1530-1565nm. In the range of 1200-1600nm, the inventive material provides high transmission and an absorbance of less than 0.2AU. In the ranges of 1525-1570 nm and 1270-1330nm the inventive material can provide an absorbance of less than 0.1 AU, and preferably less than 0.05AU, and more preferably less than or equal to 0.03AU. Embodiments of the inventive material with such low absorbance and high transmission characteristics provide an optical waveguide divide material with losses of less than 0.4dB/cm, preferably less than 0.3dB/cm, more preferably less than 0.1dB/cm, and most preferably less than 0.05dB/cm.

In some cases, even the low losses observed with these compositions may be problematic. To the extent that absorption tails or combination bands may cause loss in the 1310 or 1550nm window, hybrid materials can be made to reduce such absorption by using precursors with deuterium (deuteration) organic groups. When precursors such as $\text{CD}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{C}_6\text{D}_5\text{Si}(\text{OC}_2\text{H}_5)_5$ are employed, the siloxane

49

network becomes modified with CD_3 and C_6D_5 groups. The C-D vibrational frequencies shift to lower energies from the same C-H mode, and the overtones then are shifted as well. In this manner the overall absorbance in the near IR region can be reduced so that absorption tails are smaller, and interfering features are higher order overtones, which possess fundamentally lower intensity. The use of deuterium oxide as the water source can also minimize the effect of the SiOH absorption at 1380 nm since the absorbance position of the SiO-D is at about 2000 nm.

Finally, the above described embodiments of the invention are intended to be illustrative only. Numerous alternative embodiments may be devised by those skilled in the art without departing from the spirit or scope of the following claims.

CLAIMS

1. A planar optical waveguide formed on a substrate and comprising:
a waveguide core having a first index of refraction, and
a cladding layer formed contiguously with said core and having a
second index of refraction smaller than said first index of refraction
at least one of said core and said cladding layer being an inorganic-
organic hybrid material that comprises an extended matrix containing
silicon and oxygen atoms with at least a fraction of the silicon atoms being
directly bonded to substituted or unsubstituted hydrocarbon moieties.
2. The planar optical waveguide of claim 1, wherein the first index of
refraction is within a range of 1.4-1.55, and the second index of refraction
is within a range of 1.3-1.6.
3. The planar optical waveguide of claim 1, wherein the inorganic-
organic hybrid material has high transmission and an absorbance of less
than 0.2AU for wavelengths in a range between 1200-1600nm.
4. The planar optical waveguide of claim 3, wherein the inorganic-
organic hybrid material has high transmission and an absorbance of less
than 0.05AU for wavelengths in a range between 1525-1570nm.

51

5. The planar optical waveguide of claim 3, wherein the inorganic-organic hybrid material has high transmission and an absorbance of less than 0.05AU for wavelengths in a range between 1270-1330nm.

6. The planar optical waveguide of claim 4, wherein the absorbance within the range between 1525-1570nm is less than 0.4db/cm.

7. The planar optical waveguide of claim 5, wherein the absorbance within the range between 1270 and 1330nm is less than about 0.2 db/cm.

8. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material has a mass loss less than 6% of original mass when the material changes from a non-solid to a solid.

9. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material has a mass loss no greater than 4% of original mass when the material changes from a non-solid to a solid.

10. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material loses about 50% of its original mass prior to curing into a solid.

11. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material is deuterated.

52

12. The planar waveguide of claim 1, wherein said second cladding layer is formed over said core and wherein said waveguide includes an additional cladding layer formed between said substrate and said core.

13. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material comprises methyl-siloxane groups, phenyl-siloxane groups, and fluorine.

14. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material is provided by curing precursors comprised of polydimethyl siloxane, methyl trialkoxy silane, and phenyl trialkoxy silane.

15. The planar optical waveguide of claim 1, wherein the inorganic-organic hybrid material is provided by curing precursors comprised of PDMS, MTES, PTES, and PTFS.

16. A planar optical device formed on a substrate and comprising:
an array of waveguide cores which guide optical radiation, and
a cladding layer formed contiguously with said array of waveguide cores for confining said optical radiation to said array of waveguide cores,
at least one of said array of waveguide cores and said cladding layer being an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the

silicon atoms being directly bonded to substituted or unsubstituted hydrocarbon moieties.

17. The optical device of claim 16, wherein said device is a splitter.

18. The optical device of claim 16, wherein said device is a coupler.

19. The optical device of claim 16, wherein said device is a wavelength division multiplexer.

20. The optical device of claim 16, wherein one of said cores and said cladding layer comprises a hydrolyzed and polymerized silane selected from the group consisting of tetraalkoxysilanes, alkyltrialkoxysilanes, and aryltrialkoxysilanes.

21. The optical device of claim 20, wherein the content of the hydrolyzed and polymerized silane is at least 50%.

22. The optical device of claim 16, wherein the hydrocarbon moieties are hydrolyzed products of a modifier selected from the group consisting of inert network modifiers, active network modifiers, organic network forming modifiers, reactive polymeric modifiers and reactive polymerizable modifiers.

54

23. The optical device of claim 16, wherein the hydrocarbon moieties are unsubstituted or substituted alkyls or aryl moieties.

24. The optical device of claim 23, wherein the substituted alkyl or aryl moieties are selected from the group consisting of an amino alkyl, a hydroxyalkyl, a carboxyalkyl, and a mercaptoalkyl.

25. The device of claim 16, wherein said one of said array of cores and said cladding layer comprises the hydrolysis product of an interpenetrating organic polymeric matrix.

26. The device of claim 25, wherein there are substantially no covalent bonds between the interpenetrating organic polymeric matrix and the extended silicon-oxygen matrix.

27. The device of claim 22, wherein the hydrolyzed and polymerized product of the modifier forms an organic network that is covalently bonded via an Si-C bond.

28. The device of claim 16, wherein said one of said array of cores and said cladding layer contains fluorine.

29. The device of claim 16, wherein said one of said array of cores and said cladding layer contains an element for regulating refractive index.

55

30. The device of claim 29, wherein said element is Ge or Ti.

31. A planar optical waveguide formed on a substrate and comprising:
an array of waveguide cores in which optical radiation propagates,
a cladding layer for confining said optical radiation to said array of
waveguide cores,

said array of cores comprising a first inorganic-organic hybrid
material that comprises an extended matrix containing silicon and oxygen
atoms with at least a fraction of the silicon atoms being directly bonded to
substituted or unsubstituted hydrocarbon moieties,

said cladding layer comprising a second inorganic-organic hybrid
material that comprises an extended matrix containing silicon and oxygen
atoms with at least a fraction of the silicon atoms being directly bonded to
substituted or unsubstituted hydrocarbon moieties,

said second material having a lower index of refraction than said
first material.

32. A method for forming a planar optical device comprising the steps
of:

preparing a waveguide core composition precursor material
comprising at least one silane and a source of substituted or unsubstituted
hydrocarbon moieties,

56

partially hydrolyzing and polymerizing the waveguide core precursor material to form a waveguide core composition,

using a mold, forming an array of optical waveguide cores comprising said waveguide core composition, and

5 completing hydrolysis and polymerization of the waveguide core composition under conditions effective to form an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon atoms being directly bonded to said substituted or unsubstituted hydrocarbon moieties.

10 33. The method of claim 32, wherein the mold permits the step of forming an array to include forming structures having a resolution of less than 1 micron.

15 34. The method of claim 32, wherein the mold permits the step of forming an array to include forming structures having a resolution less than 0.6 microns.

20 35. The method of claim 32, further comprising the step of choosing the mold to be an intaglio imaging plate.

36. The method of claim 32, wherein the step of forming an array further comprises:

57

- (a) loading a negative master with said waveguide core composition;
- (b) compressing the negative master and waveguide core composition against a substrate and simultaneously curing the waveguide core composition; and
- (c) releasing the negative master from the core composition.

37. The method of claim 32, wherein the step of forming an array further comprises:

- (a) covering a plate with cladding material;
- (b) using a positive master, forming depressions in the cladding material;
- (c) loading said waveguide core composition into the depressions;
- (d) compressing the waveguide core composition and cladding material against a substrate and simultaneously curing the core composition and cladding material; and
- (e) releasing the plate from the core composition and cladding material.

38. The method of claim 37, wherein curing further comprises thermally curing.

58

39. The method of claim 37, wherein curing further comprises curing with light and selecting at least one of the substrate and the plate to be transparent.

5 40. The method of claim 32, wherein the step of forming an array further comprises:

- (a) covering a plate with cladding material;
- (b) loading said waveguide core composition into a negative master;
- 10 (c) adhering said waveguide core composition to the cladding material;
- (d) compressing the waveguide core composition and cladding material against a substrate and simultaneously curing the core composition and cladding material; and
- 15 (e) releasing the plate from the core composition and cladding material.

41. The method of claim 40, further comprising after the step of adhering; overcoating the core composition and cladding material with an
20 additional layer of cladding material.

42. The method of claim 40, wherein the step of adhering further comprises contacting said waveguide core composition and cladding

material while simultaneously curing said waveguide core composition and cladding material.

43. The method of claim 40, wherein the step of curing comprises thermally curing.

44. The method of claim 40, wherein the step of curing further comprises curing with light and selecting at least one of the substrate and the plate to be a transparent material.

45. The method of claim 32, wherein the step of forming an array further comprises:

- (a) coating a substrate with cladding material;
- (b) partially curing the cladding material;
- (c) pressing an embossing element into the partially cured cladding material;
- (d) curing the embossed cladding material;
- (e) filling the embossed cladding material with the waveguide core composition; and
- (f) curing the waveguide core composition.

46. The method of claim 45, wherein curing further comprises thermally curing.

60

47. The method of claim 45, wherein curing further comprises curing with light and selecting of the substrate and be transparent.

48. The method according to claim 32, wherein the waveguide core composition precursor material comprises PDMS, MTES, and PTES.

49. The method of claim 32, wherein the waveguide core composition precursor material comprises MTES, DPDMS, and PTES.

50. The method of claim 32, wherein the waveguide core precursor material comprises MTES, PTES, PDMS, and PTFS.

51. The method of claim 32, further comprising the steps of:

forming a cladding layer on said array of waveguide cores according

to a method comprising the steps of:

(a) preparing a cladding composition precursor material comprising at least one silane and a source of hydrocarbon moiety,

(b) partially hydrolyzing and polymerizing the cladding composition precursor material to form a cladding composition,

(c) applying by liquid phase deposition a coating of said cladding composition to said patterned array of waveguide cores, and

(d) drying said cladding composition to form a cladding layer on said array of waveguide cores.

52. The method of claim 51, wherein said cladding layer comprises an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon atoms being directly bonded to substituted or unsubstituted hydrocarbon moieties.

53. The method of claim 51, wherein said cladding composition precursor material comprises PDMS, MTES, PTES, or combinations thereof.

54. The method of claim 51, wherein the cladding composition precursor material comprises MTES, DPDMS, PTFS, or combinations thereof.

55. The method of claim 51, wherein the cladding composition precursor material comprises MTES, PTES, PDMS, PTFS, or combinations thereof.

56. A method for forming a planar optical device on a substrate comprising the steps of:

forming an array of waveguide cores, and

62
forming a cladding layer on said array of waveguide cores by the steps of:

- (a) preparing a cladding composition precursor material comprising at least one silane and a source of hydrocarbon moiety,
- (b) partially hydrolyzing and polymerizing the cladding composition precursor material to form a cladding composition,
- (c) applying by liquid phase deposition a coating of said cladding composition to said array of waveguide cores, and
- (d) drying said cladding composition to form a cladding layer on said array of waveguide cores.

57. The method of claim 56, wherein the cladding layer comprises an inorganic-organic hybrid material that comprises an extended matrix containing silicon and oxygen atoms with at least a fraction of the silicon atoms being directly bonded to substituted or unsubstituted hydrocarbon moieties.

58. The method of claim 56, wherein said array of cores is patterned by etching unmasked portions of a core layer.

59. A method for forming a cladding layer on a substrate in a planar optical device comprising the steps of:

63

- (a) preparing a cladding composition precursor material comprising at least one silane and a source of hydrocarbon moiety,
- (b) partially hydrolyzing and polymerizing the cladding composition precursor material to form a cladding composition,
- (c) applying by liquid phase deposition a coating of said cladding composition to said substrate, and
- (d) drying said cladding composition to form a cladding layer on said substrate.

60. A method for forming a planar optical waveguide device comprising the steps of

- (a) depositing a first clad layer on a substrate,
- (b) imprinting a pattern of grooves in said first clad layer by applying a positive master to said first clad layer,
- (c) doctoring waveguide core composition material into said grooves to form waveguide cores,
- (d) depositing a second clad layer over said first clad layer and said waveguide cores.

61. The method of claim 60, wherein the positive master is compressible and comprising a film or foil on a flexible backer and wherein the master is applied by rolling against said first clad layer.

64

62. The method of claim 60, further comprising curing the waveguide core.

5 63. The method of claim 62, wherein the step of curing comprises curing with light and further comprising selecting at least one of the substrate and the master to be a transparent material.

10 64. A method for forming a planar optical waveguide device comprising the steps of

- (a) filling a pattern of grooves in a negative master with a waveguide core composition material,
- (b) applying the negative master to a substrate,
- (c) removing the master so as to transfer the waveguide core composition material to the substrate to form a pattern of waveguide cores, and
- (d) forming a cladding layer over said pattern of waveguide cores.

20 65. The method of claim 64, wherein the negative master is compressible and comprises a film or foil on a flexible backer and wherein the master is applied by rolling against said substrate.

65

66. The method of claim 64, further comprising curing the waveguide composition during the step of applying the negative master to the substrate.

5 67. The method of claim 66, wherein the step of curing comprises curing with light and further comprising selecting one of the substrate and the master to be a transparent material.

1 / 8

FIG.1

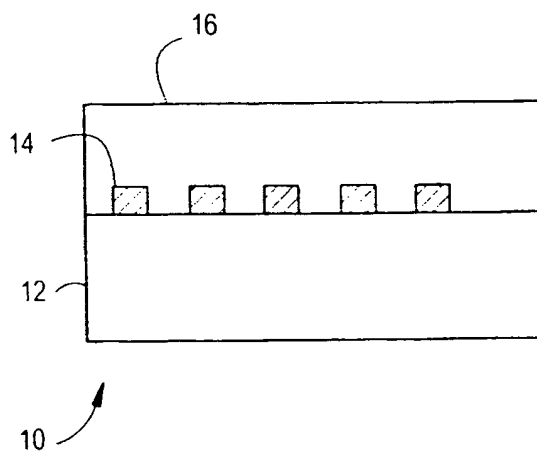
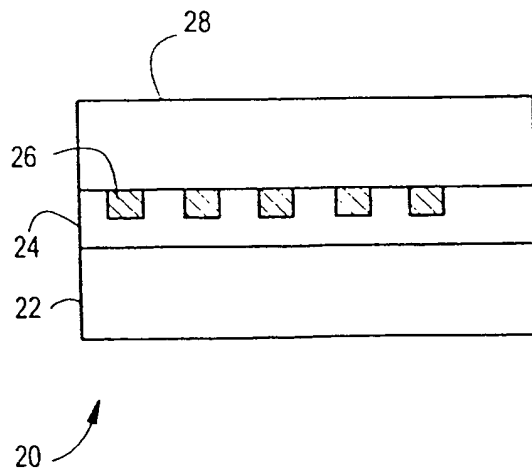


FIG.2



2 / 8

FIG.3A

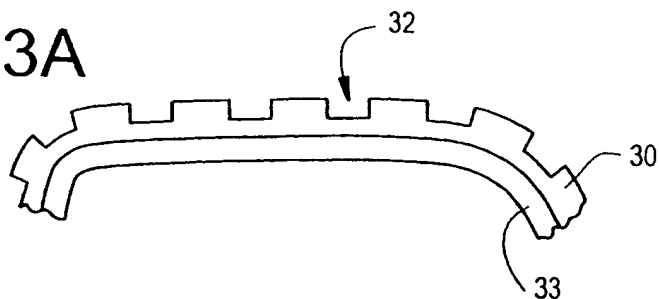


FIG.3B

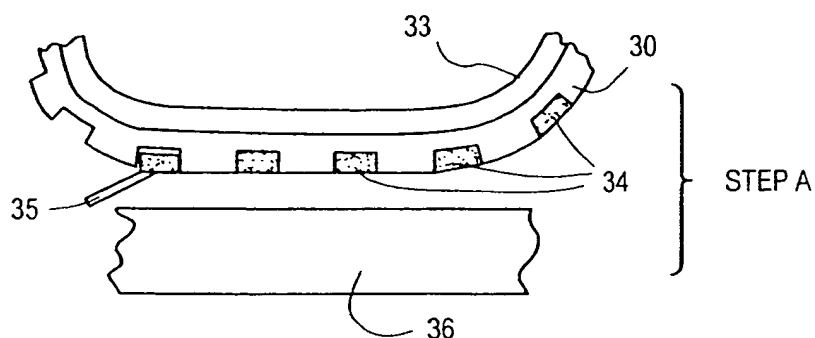


FIG.3C

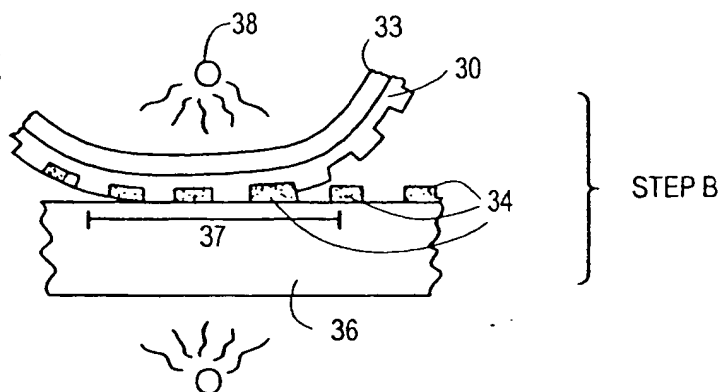


FIG.3D

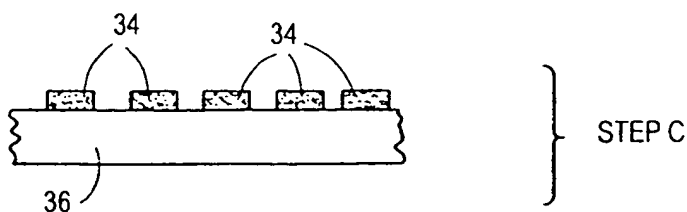
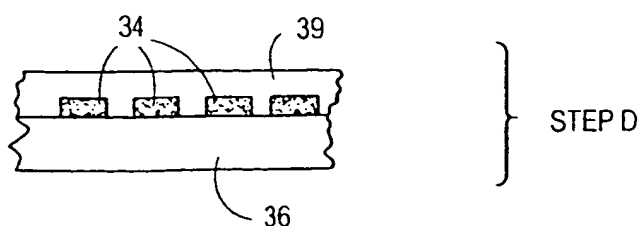


FIG.3E



3 / 8

FIG.3F

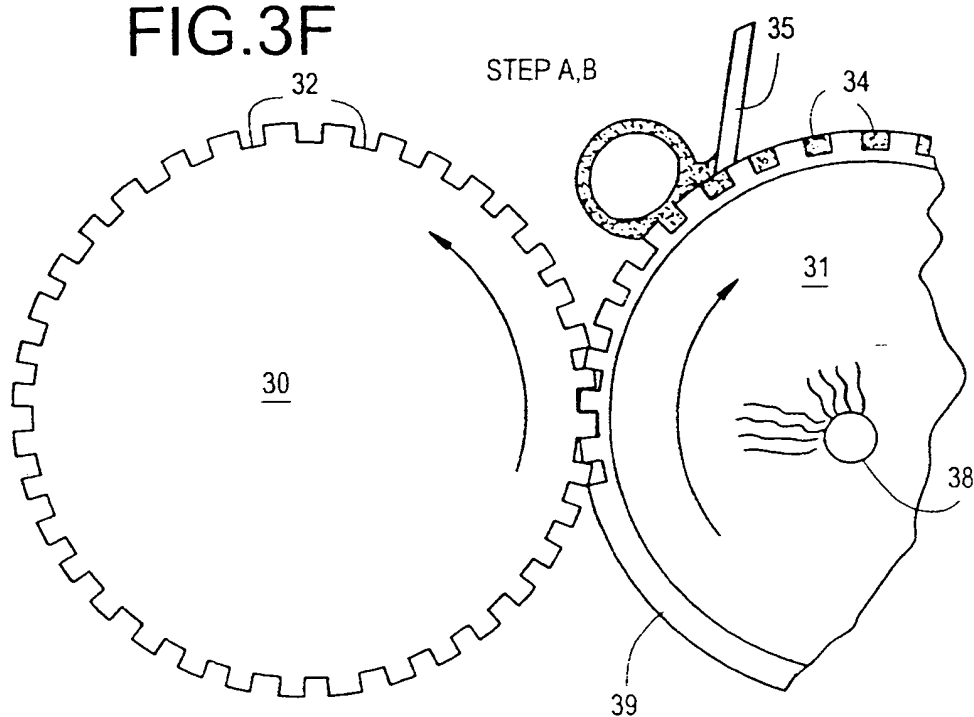


FIG.3G

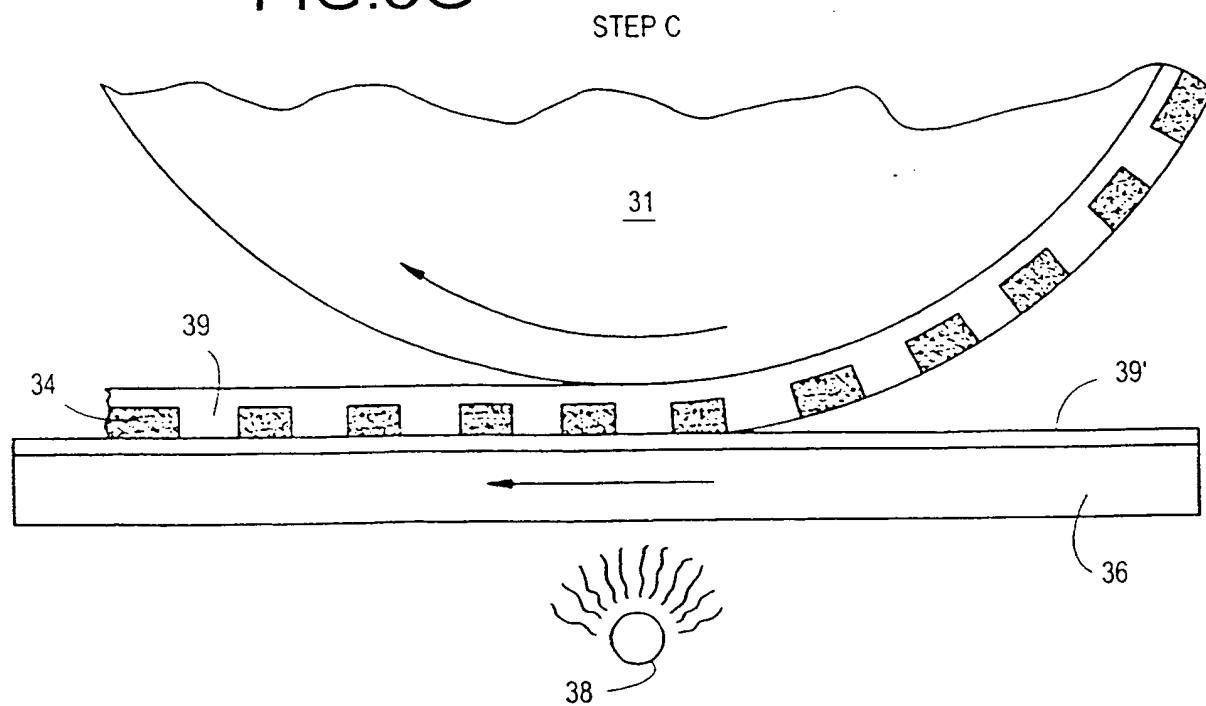


FIG.3H

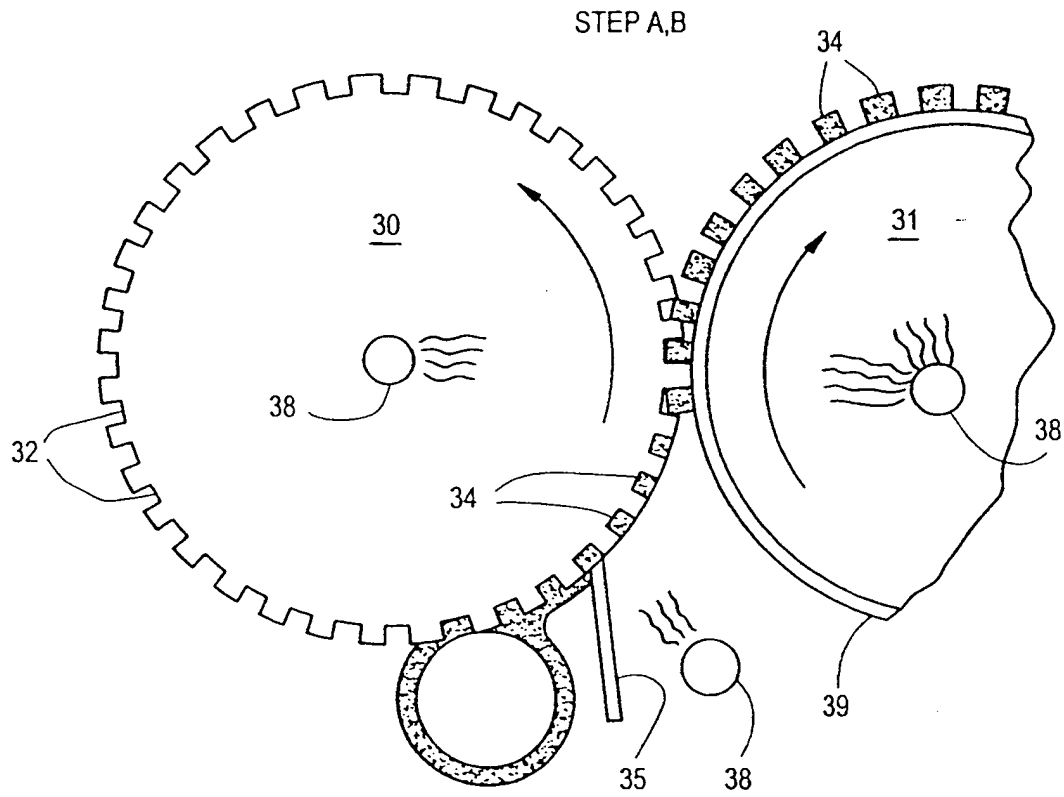
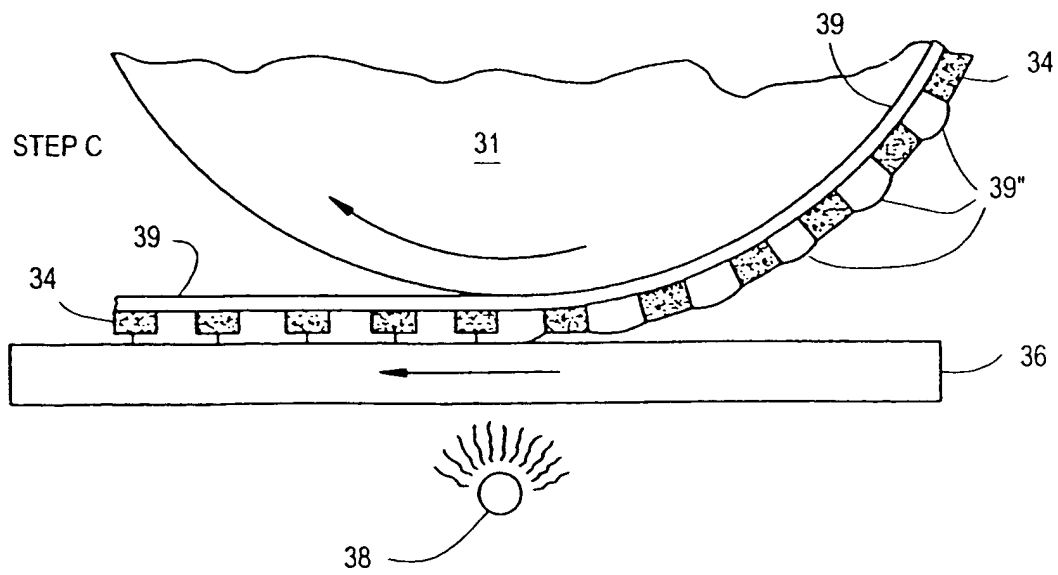


FIG.3I



SUBSTITUTE SHEET (RULE 26)

5 / 8

FIG.4A

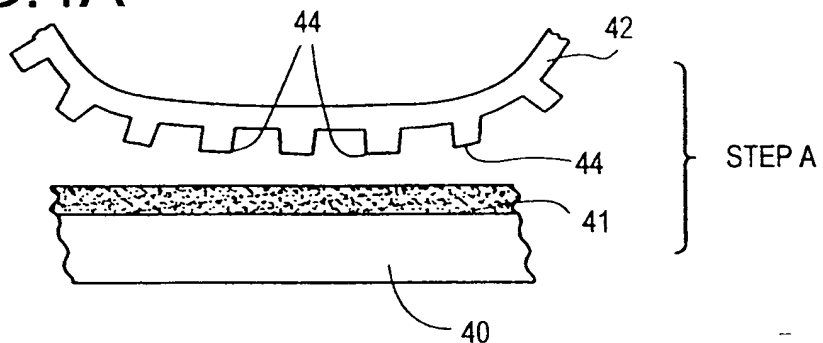


FIG.4B

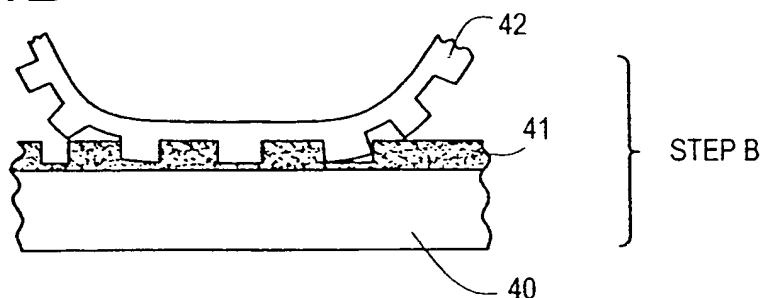


FIG.4C

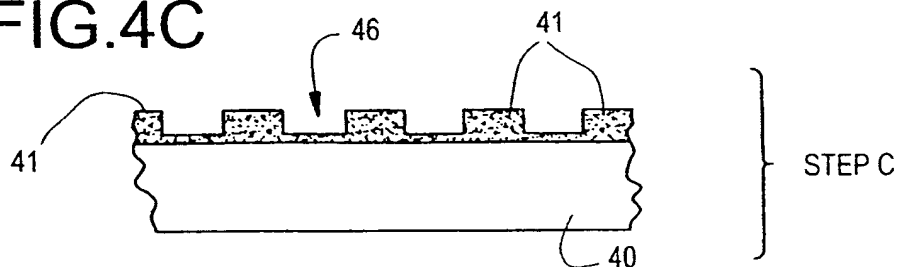


FIG.4D

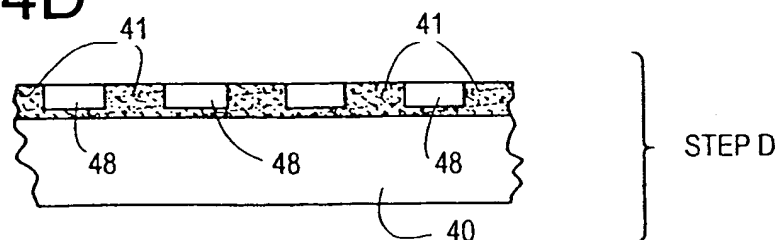
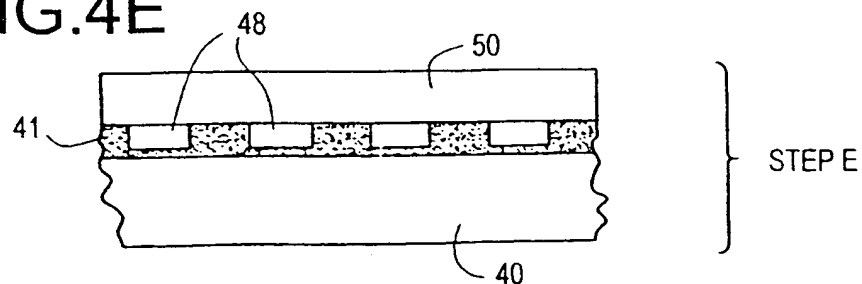
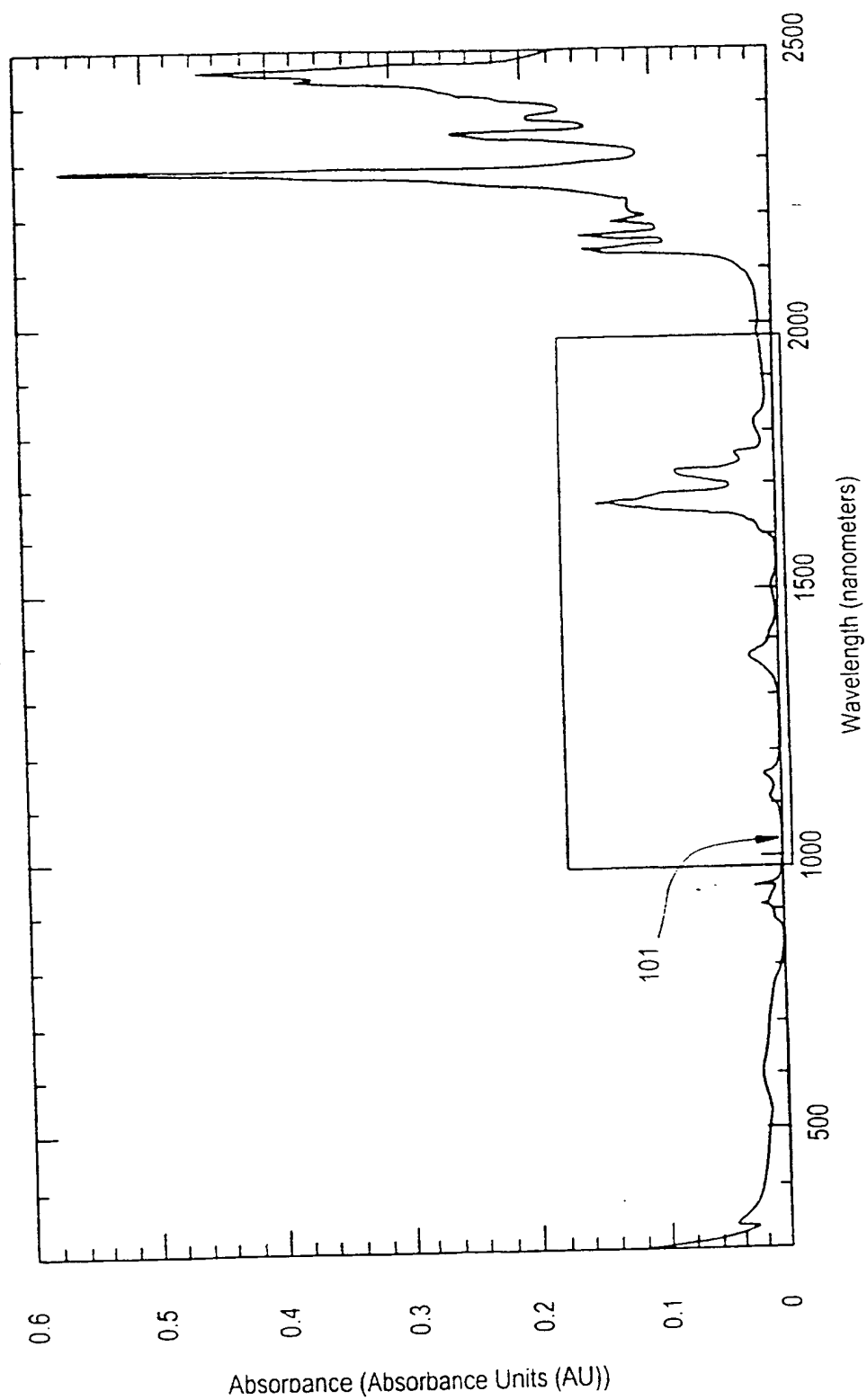


FIG.4E



6 / 8

FIG. 5



7 / 8

FIG. 6

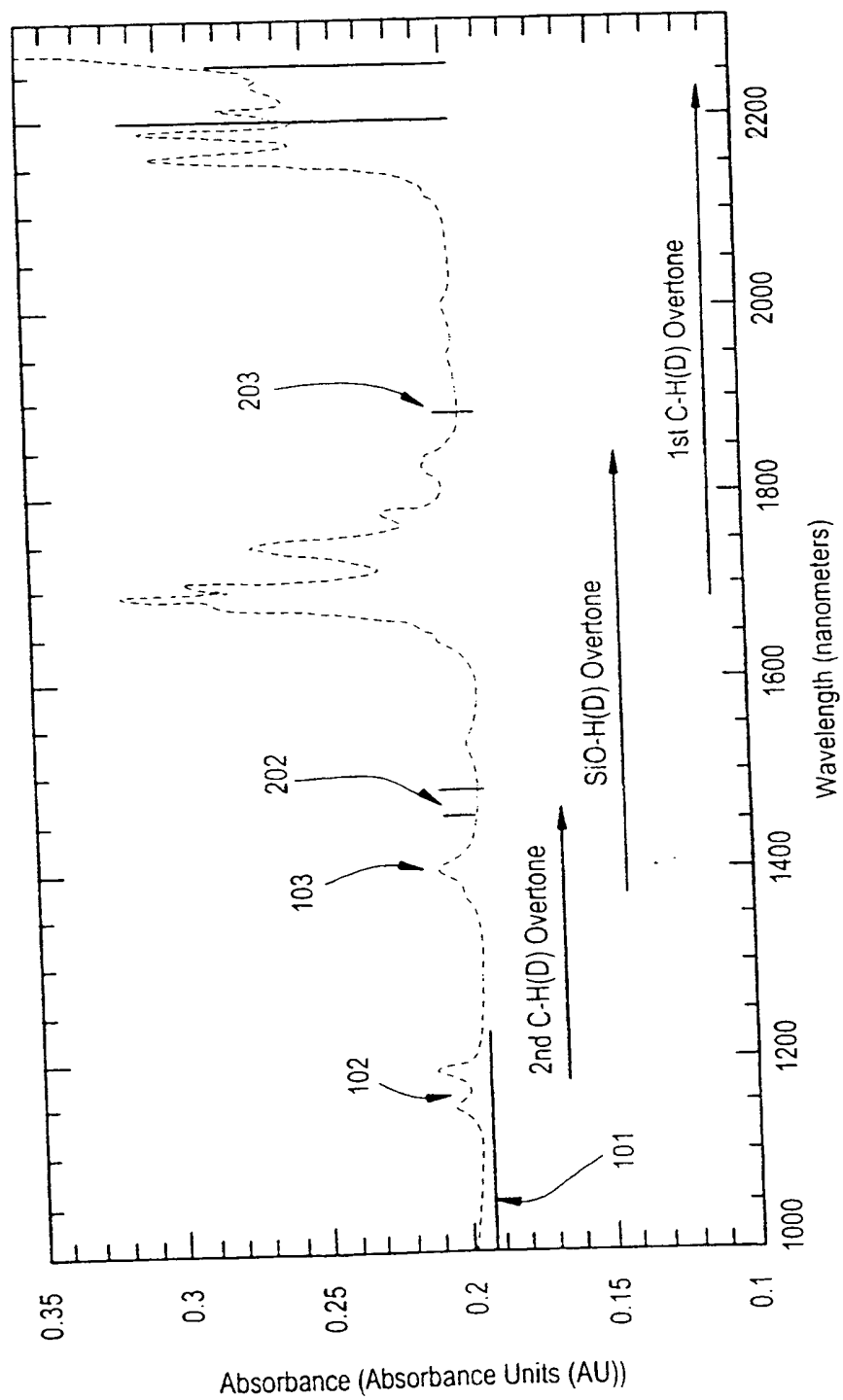
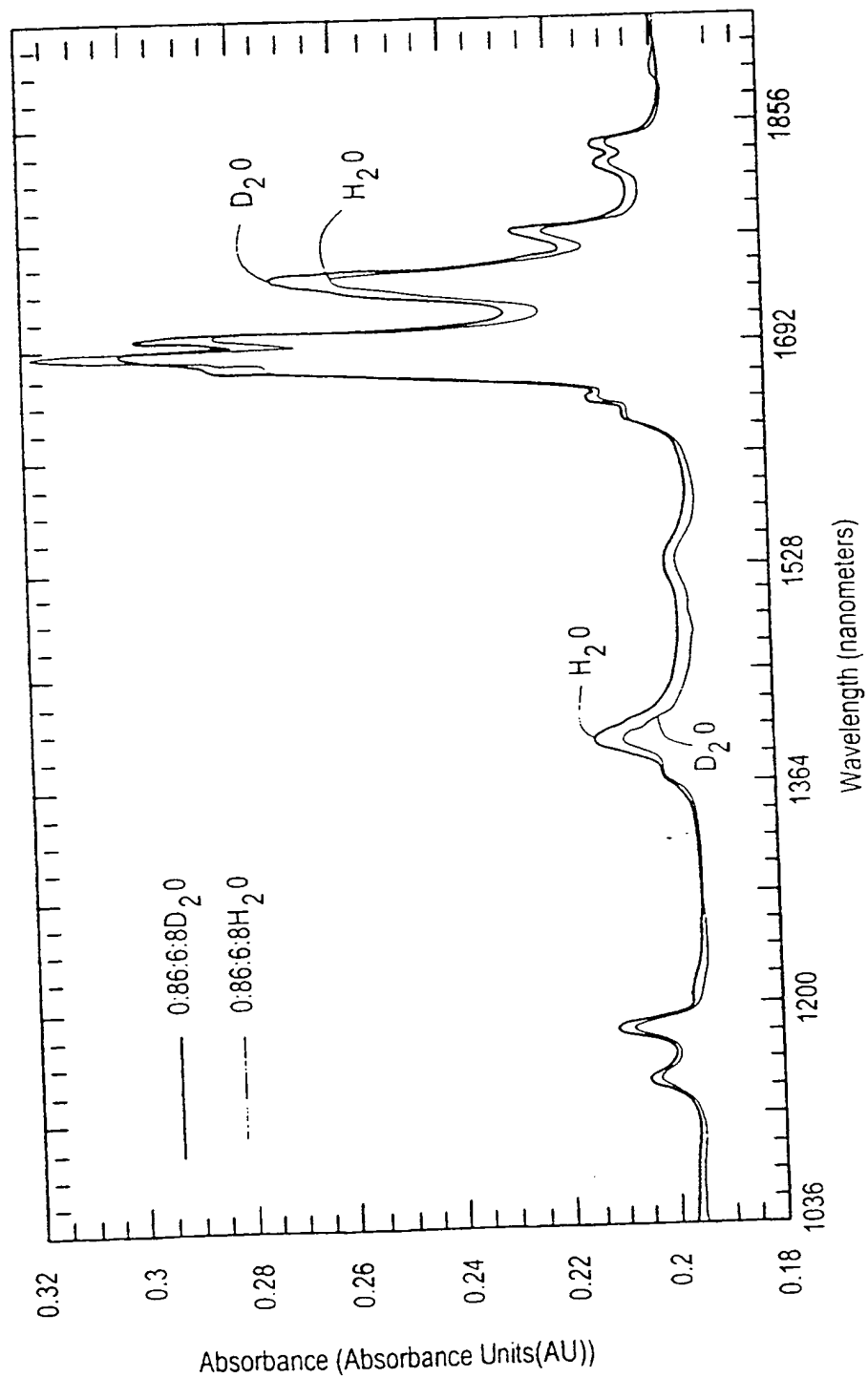


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/22760

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G02B 6/10; C03B 37/022

US CL :385/129, 132; 65/386; 528/25; 525/474

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 385/129, 130, 131, 132; 65/386; 528/25; 525/474

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: core#, organi inorganic, hydrocarbon

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 5,686,548 A (GRAINGER ET AL) 11 November 1997 (11/11/97), see entire document, especially column 13, lines 49-54.	1
A	US 5,480,687 A (HEMING ET AL) 02 January 1996 (02/01/96), see columns 3, 4, and 9.	1-67
A	US 5,481,633 A (MAYER) 02 January 1996 (02/01/96), see entire document.	36-46



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

02 FEBRUARY 1998

Date of mailing of the international search report

23 FEB 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

HEMANG SANGHAVI

Telephone No. (703) 305-3484

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US97/22760**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/22760

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-31, drawn to a planar optical waveguide, classified in class 385, subclass 129.

Group II, claims 32-67, drawn to a method of forming a planar optical waveguide, classified in class 65, subclass 386.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the claim of these groups are directed to different inventions which are not so linked to form a single general concept. The claims in the different groups do not have in common the same or corresponding "special technical features". In particular the planar optical waveguide of Group I is completely different from that of Group II including method of manufacturing the planar optical waveguide.